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ANALYSIS OF THE COMPOSITION OF THE ATMOSPHERE IN THE LOS ANGELES BASIN

John R. Ehrenfeld

Abcor, Incorporated

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ANALYSIS OF THE COMPOSITION OF THE ATMOSPHERE IN THE LOS ANGELES BASIN

by

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16. ABSTRACT

A material balance model and an inversion technique was developed that appear to produce reasonable estimates of the contribution of different emission sources in the Los Angeles atmosphere. Different sources exhibit very characteristic diurnal and daily patterns. The automobile exhaust contribution to the hydrocarbon burden on weekdays was found to be different from that on weekends. Estimates of the loss of reactive compounds such as ethylene and propylene were made and these compare favorably with smog chamber data. Recommendations for future field trip studies are made since difficulty was encountered in interpreting the data.

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SECTION I

CONCLUSIONS

The principal conclusions that can be drawn from this study are as follows:

1. The material balance model and inversion technique appear to produce reasonable estimates of the contributions of different emission sources to the atmosphere, and, can with improvements provide a means of deducing source behavior from atmospheric data directly, without application of reactive simulation dispersion models.

2. The selection of potential sources, exhaust, spillage, evaporation, natural gas seepage, special methane and special propane, appears reasonable. Excellent fits to the atmospheric data are achieved for all 24 conservative hydrocarbon species with only six independent variables. The special methane source appears to be a consequence of natural methane background in the air mass entering the Basin. The apparent source of propane can not be so related to a natural or man-made source.

3. The different sources exhibit very characteristic diurnal and daily patterns. Exhaust is higher on weekdays than weekends by almost an order of magnitude, as would be expected in relation to traffic density patterns. The weekday source strength peaks about 0830 and falls off more slowly than does the traffic density, indicating a build-up of hydrocarbons in the morning when atmospheric mixing is limited. The week-end pattern does not show a similar peaking.

4. Estimates of loss of reactive species can be made. Estimates of the loss of ethylene and propylene differ by the same order of magnitude as do the reactivities of the two species in laboratory experiments. Lack of independent data on gasoline and exhaust composition limited the reactive loss estimates to only a few species.

5. The contribution of the auto exhaust to the non-methane hydrocarbon content of the atmosphere is the dominant element during the peak weekday traffic period. The other sources also appear to be significant, and are of the same order of magnitude or even greater at nonpeak times.

6. The absolute values of the derived source strengths agree reasonably with estimates of emissions derived from automobile density and average emission factors.

7. The normalizing technique used to adjust data from varying times in which all sources were referred to the natural gas apparent strength, appears to reduce considerably the variability of the data due to atmospheric randomness.

SECTION II

RECOMMENDATIONS

The following recommendations for future considerations are made:

1. In future sampling programs, data on gasoline composition should be gathered at the same time the program is run.

2. Additional work be done to develop a better understanding of the correlative relationships connecting the observed data and derived source parameters with atmospheric parameters and source characteristics.

SECTION III

INTRODUCTION

GENERAL

There is a considerable body of work concerned with elucidating the mechanisms and processes involved in the formation of photochemical smog. These studies may be broadly grouped into three main areas of interest:

1. Chemistry of photochemical reaction involving hydrocarbons,
2. Models for describing pollutants behavior, particularly in this case, in the Los Angeles Basin, and
3. Source characteristics of the Basin.

The objectives of this study are primarily directed toward the third topic, i.e., to identify and characterize the sources contributing to the measured composition at the downtown Los Angeles and Huntington Park sampling sites, and to determine the relative contribution of each source type. In addition, relationships connecting the important pollutant species to the sources and to the state of the atmosphere (meteorology) are to be sought.

One approach to develop these relationships would be to develop a deterministic model containing a mathematical analog to the physical and chemical process occurring. Such models have been developed for the Los Angeles Basin (1, 2, 3). This study is <u>not</u> such a development. We have sought instead to extract the statistical information contained in the compositional data available for analysis and utilize it to derive empirical relationships.

SOURCES OF DATA

Detailed hydrocarbon and other pollutant gaseous species data have been collected in Los Angeles over several years. One such set of data was collected in the fall of 1968. The objective of this project was to examine the composition data and concommitant meterological data in order to develop a description of the atmosphere of the Los Angeles Basin and of its reactive character. Diurnal patterns were to be identified.

The data were collected at two sites. One site was located in downtown Los Angeles (DOLA), at which the EPA was responsible for data collection and analysis. The second site was located at Huntington Park. Scott Research Laboratories was responsible for the data collection and analysis at that site.

The EPA mobile laboratory data include chemical analyses for about 60 chemical species on approximately 330 air samples. They include a variety of paraffinic, olefinic, aromatic and acetylenic hydrocarbons, nitrogen dioxide, nitric oxide, and carbon monoxide. Samples were collected over a 50-minute period, eight samples per day (5:00 a.m. - 3:00 p.m.) for 41 days between September and November 1968. Approximately 10 additional samples were collected along roadways at a later date (1970) to provide a basis for estimating the composition of auto exhaust emitted into the Los Angeles atmosphere. In the 1968 series other data were obtained at DOLA by the Los Angeles Air Pollution Control District including analyses for carbon monoxide, total hydrocarbon, nitric oxide and nitrogen dioxide. In addition, ultraviolet light dosage, oxidant, temperature, total hydrocarbon, and nitrogen oxides have been averaged for four-hour intervals between 7:00 a.m. and 7:00 p.m. The Scott Research Laboratories has reported analyses of approximately 103 air samples taken at the Huntington Park, California site at various times between October and November 1968 (4). The hydrocarbon analyses of Scott, however, were obtained by instantaneous sampling of the atmosphere.

OBSERVED SOURCE BEHAVIOR

As noted, a principal set of objectives is related to the identification of sources. Automobiles contribute most of the photochemically active species to the Basin (5). This source alone cannot, however, account for all of the hydrocarbon species found in atmospheric samples collected by a number of investigators. Neligan found that the low boiling hydrocarbons could not be accounted for by automotive exhaust alone and suggested natural gas as a probable additional significant source (6). He also suggested contributions by blowby and evaporative losses from carburetor and the gasoline tank.

Stephens and Burleson note further that natural gas alone cannot explain the excessive ratio of propane to ethane and methane, and suggest that evaporation of the light ends from gasoline may be the source (7). In a later study, Gordon, et.al., note the same sort of patterns as Stephens and Burleson (8). They also note that the ratios of exhaust hydrocarbons measured in the atmosphere do not agree with those obtained on tests based on the California test cycle.

Lonneman, et.al., in a study of aromatic hydrocarbons in the L.A. atmosphere found that toluene levels were too high to be associated only with automotive emissions and suggest solvent evaporation as a possible source (9). Scott in their analysis of the data to be used in this study also note that auto exhaust (based on carbon monoxide levels) is the major source reflected in their measurements (4). They find, as in the earlier works referred to above, that the light hydrocarbons (C_1-C_3) must come from other sources.

These studies plus reference to the source inventory of the L.A. Basin (5) suggest that initially all the following potential sources should be included in our analysis:

1. Automobile exhaust
2. Automobile evaporation and blowby
3. Solvent evaporation
4. Natural gas
5. Stationary combustion (NO)
6. Process emissions (CO)

Other sources of hydrocarbons such as refinery emissions and aircraft exhaust do not appear, *a priori*, to be significant.

As will be shown in detail below, this analysis was based principally on hydrocarbon emitters, so that the last two sources were not relevant. Further solvent evaporation was not included for the following two reasons. First, the magnitudes of solvent emission in Los Angeles, although not negligible, is small compared to the emission associated with gasoline(5). Secondly, solvents represent such a varied composition spectrum, that it would have been very difficult to define a representative hydrocarbon species spectrum. The approach is deficient in this regard, and refinements in the future should include consideration of solvents. Six potential source sub-groups were postulated. These were:

1. Automobile exhaust
2. Gasoline evaporation
3. Gasoline spillage
4. Natural gas seepage
5. Methane source
6. Propane source

The first four are, in essence, included in the *a priori* list above. It appeared important to separate gasoline loss into two components, evaporation and spillage reflecting the different compositions of the two. In evaporation losses (carburetor hot soak, etc.), the vapor would be enriched in the more volatile species, (10) whereas spillage would result in a source resembling the full compositional spectrum of gasoline (11).

The latter two sources were added to the list during the study to treat what appeared to be an anomalous behavior pattern of methane and propane with respect to the first four sources. Assuming a realistic methane and propane composition for the first four sources, the initial analysis generated results that did not appear reasonable. The composition data indicate the existence of a quantity of methane and of propane that must arise from sources other than the four included herein. It was expedient to segregate the uncertainty as to the nature of this unknown source factor into a separate term for propane and methane.

SECTION IV

THEORETICAL APPROACH

MATERIAL BALANCE MODEL

An understanding of the behavior of the sources of hydrocarbons is, per se, important in understanding and controlling photochemical smog. Since photochemical smog formation is produced by a dynamic set of processes, relative to the general dispersive mechanisms simultaneously taking place, detailed understanding of diurnal and day-to-day patterns of behavior is necessary in statistical analysis of observed oxidant levels and in providing realistic inputs to dynamic, reactive models.

Such dynamic models have been the subject of intensive development, and hold great promise in being able to simulate conditions which have been observed leading to verification of theory, and in predicting smog levels for hypothetical cases. These models, in essence, represent a transformation of the emissions of various hydrocarbon species, through kinetic and dispersive processes, into ambient pollutant concentration perceived by measurement.

Previous analyses of observed data have been carried out by applying such models or by using fairly insensitive techniques based on ratios of species to key or conserved components. The first approach has been unsuccessful in isolating detailed source behavior, largely due to the complexities of applications of reactive models (3). The second approach has provided more general understanding to source behavior, but is limited by the uncertainty in the measurements and by the scatter introduced by dispersive randomness (4, 8, 12).

Our approach, outlined below and applied as shown in later sections, is an attempt to find an intermediate technique, which falls between the simple ratio-analysis and complex simulation modeling. The basic model on which this whole analysis is set is that the measured concentration of certain non-reactive (conserved) hydrocarbon species can be related in a deterministic, integral way to the sources of these species. The relationship takes the form of material balances, assuming that the entire basin or at least the air parcel being sampled can be modeled as a variable volume chemical reactor, as has been discussed by Friedlander and Seinfeld. (13) The general form of the material balances equation is:

$$C_i = \frac{1}{V} \sum_{j=1}^{N} \varepsilon_{ij} Q_j \quad i = 1, 2....M \qquad (1)$$

where C_i = measured atmospheric concentration of the i^{th} hydrocarbon species

V = the volume in which the source emissions have been mixed

Q_j = emission source strength of the j^{th} source

ε_{ij} = a stoichiometric coefficient for the i^{th} species from the j^{th} source

Appropriate units for these quantities are introduced in the detailed discussion below. Emission source strength is a measure of the total quantity of hydrocarbon added to the volume being sampled, as for example, gallons of gasoline, or kilograms of natural gas, etc. The stoichiometric coefficient gives the fraction of a particular species in the source, for example, as ppm or mole fraction butane in natural gas or exhaust.

The size of the characteristic volume cannot be deduced directly from the data, so that the working formula is modified by redefining the source strength according to the following equations:

$$C_i = \sum_{j=1}^{N} \epsilon_{ij} Q'_j \qquad i = 1, 2....M \qquad (2)$$

$$Q'_j = Q_j/V \qquad (3)$$

Now, if the concentrations and stoichiometric factors are known, it should be possible to invert the system of material balance equations to determine the unknown source terms, Q'_j. If there are fewer conservative components than sources ($N < M$), the equations cannot be solved. If the two are equal, then a single algebraic solution exists. If there are more components than sources ($N > M$), then the equations do not have a unique algebraic solution, but can be solved by statistical techniques to find the best-fitted source values.

There appear to be some 10 to 11 species in the Scott and DOLA field data which have zero or very low reactivity, and another 10 to 20 of low reactivity, so that there may be up to 30 such conservative equations. Important sources number only six (6) and are as noted earlier (automotive exhaust, evaporative losses, spillage losses, natural gas leakage, and "unknown" methane and propane sources). The essential feature of the system of material balance equations (relative to a ratioing technique) is that a solution for the Q'_j terms utilizes all of the information contained in the 25 to 30 species measurements and compresses it into a new set of only a few variables. Because this transformation of variables is performed in a least-square sense, the effect of individual measurement errors is minimized. Consequently the new variable should be statistically more reliable than the basic concentration values, provided the basic model is realistic.

The derived source strength can be used to estimate the degree of reaction for the active species. Using the derived source strengths, a similar set of material balances would give predictions of the concentration of the reactive species assuming an absence of reactions, viz.:

$$\xi_k^\circ = \sum_{j=i}^{N} \varepsilon_{ij} Q_j' \qquad k = 1, 2, \ldots L \qquad (4)$$

where ξ_k° = unreacted concentration of reactive species.

There are some 20 to 30 compounds that would be considered as reactive species. Thus, a comparison of the predicted concentrations with the measured values provides a direct estimate of the photochemical reaction of each species.

The fraction, f_k, represents the degree of reaction, as

$$f_k = \frac{\xi_k^\circ - \xi_k}{\xi_k^\circ}$$

where ξ_k = the measured concentration of the k^{th} species.

Plots of averaged (over different days) values of f_k versus time of day should show the significance of reactivity groupings, in the sequence illustrated below in Table 1 (14) or according to some other set (15). Difficulty in estimating the composition of the sources, particularly for the reactive species, has limited the analysis of reactive species to two compounds, ethylene and propylene.

The material balance approach differs from other studies (4, 8, 12) which attempt to follow the reaction by examining ratios of a single reactive species to a non-reactive species. Since, in general, more than one source contributed to the atmosphere over the time that reaction is occurring, the ratio may lead to erroneous estimates of reaction, if the

TABLE 1.

REACTIVITY OF HYDROCARBONS GROUPED ACCORDING
TO RELATIVE HYDROCARBON CONSUMPTION REACTIVITY

Group	Classes of Compounds	Specific Species
1.	C_1-C_5 paraffins, acetylene, Benzene	Methane, ethane, acetylene, propane, isobutane, butane, pentane, isopentane, cyclopentane, benzene (10+1 (CO) = 11 species).
2.	C_6 + paraffins	Hexane, heptane...undecane; substituted butanes and pentanes...19 species.
3.	Toluene, other monoalkylbenzenes	Toluene, ethylbenzene, o,m, p-xylenes, propylbenzenes, 2,3 and 4-ethyltoluenes, etc. (14 species).
4.	Ethylene	Ethylene
5.	Dialkyl- and Trialkylbenzenes	1,3,5 and 1,2,4-trimethylbenzenes (2 species).
6.	1-alkenes	Propylenes, butenes, 1-pentene, cyclopentene, 1-hexene, etc. (7 species).
7.	Internally double-bonded alkenes	Cis and trans 2-pentene, 2-methyl 2 butene, cis and trans 3-hexene, cis and trans 2-hexene (7 species).

relative strengths of the sources vary over the period (as, is noted later, appears to be the case). (4, 12) After inverting the material balances relating the composition for each data set to the sources identified above, further analysis is performed using suitably averaged sets of the source strengths, not on averaged sets of the compositional data, per se, as in Eschenroeder and Martinez (3, 12).

Prior to the analysis the basic equations (Eq. 1) were transformed to be consistent with the units of concentration and composition. The atmospheric composition data are expressed as ppb, the components of exhaust are expressed as ppm, as is customary, while components of gasoline, both spillage and evaporation, and natural gas are expressed as mole fractions. It is convenient to consider the volume of air over a one-square meter area. The material balance, equivalent to Equation 1, is:

$$C\left[\frac{PL}{R_g T} \times 10^{-9}\right] = \frac{1000R_v}{MW_v}\,\varepsilon_v + \frac{1000R_s}{MW_s}\,\varepsilon_s + \frac{1000\,R_{ng}}{MW_{ng}}\,\varepsilon_{ng} + 16\left(\frac{1000R_x}{MW_x}\right)(\varepsilon_x) \times 10^{-6} + \frac{1000R_m}{MW_m}\,\varepsilon_m + \frac{1000R_p}{MW_p}\,\varepsilon_p \qquad (6)$$

where C = concentration in ppb

P = atmospheric pressure in atm

L = mixing height in meters

T = ambient temperature in °K

R_g = gas constant ($87.06 \times 10^{-6}\ \frac{m^3 - atm}{mol - °K}$)

$R_v, R_s, R_{ng}, R_x, R_m, R_p$ = source strength in kg/m^2 for gasoline evaporative, spillage, natural gas, exhaust, methane and propane sources, respectively.

$\varepsilon_v, \varepsilon_s, \varepsilon_{ng}, \varepsilon_m, \varepsilon_p$ = stoichiometric coefficient for evaporative, spillage natural gas, methane and propane sources respectively, in mole fraction

e_x = stoichiometric coefficient in exhaust in ppm.

MW_v, MW_s, MW_{ng}, MW_x, MW_m, MW_p = molecular weight of vaporization, spillage, external gas, exhaust methane and propane sources, respectively.

The factor of 16 in the exhaust term represents the combined gasoline plus combustion air at the typical air/fuel ratio of 15. Molecular weight for the spillage and evaporative sources are essentially equal to the value for gasoline; a value of 100 has been used. Exhaust molecular weight is about 28, and the value for natural gas is about 16. The factor 10^{-9} on the left hand side converts ppb to volume per volume, as does the factor 10^{-6} in the exhaust term. If we further define dimensionless source strengths, R', by the following equation:

$$R' = R \times \frac{R_g T}{PL} \times 10^{10} \qquad (7)$$

We obtain the equations that were used in computer runs. The output of the computer runs provided values of R', which we denote <u>apparent source strength</u>, for the several sources. The fifth term on the right, that for methane, only appears in the material balance for methane, i.e., the stoichiometric coefficient is unity for methane and zero for all other components. The propane source term, similarly appears only in the propane material balance. The form of the equation (there will be one such equation for each conservative component) is:

$$C = \varepsilon_v R'_v + \varepsilon_s R'_s + \varepsilon_{ng} R'_{ng} + 5.72 \times 10^{-5} \varepsilon_x R'_x + \varepsilon_m R'_m + \varepsilon_p R'_p \qquad (8)$$

The inversion procedure used is based on the method of least squares as is described by Whittaker and Robinson (16). The overdetermined set of equations can be reduced to a consistent set of linear equations which minimize the sum of weighted residual square errors. Solution of this set of equations (termed the normal equations) for the source strengths (Q's) is a standard problem in matrix algebra. A version of the BIOMED statistical analysis program, available in the CDC Cybernet, was used for the numerical analysis.

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The BIOMED software package consists of an extensive group of statistical analysis computer programs originally developed at UCLA for medical research purposes. The functions performed by these programs were well suited to the processing requirements for analysis of the Los Angeles Basin data and could be applied without developing alternative analytic programs. The programs accept information directly from punched cards and can be selectively called into execution by a simplified control card procedure.

The programs are arranged in the six main groups of which two were employed as listed below. Not all of the separate programs were used.

Class R - Regression Analysis

1. Simple Linear Regression
2. Stepwise Regression
3. Multiple Regression with Case Combinations
4. Periodic Regression and Harmonic Analysis
5. Polynomial Regression
6. Asymptotic Regression

Class V - Variance Analysis

1. Analysis of Variance for One-Way Design
2. Analysis of Variance for Factorial Design
3. Analysis of Covariance for Factorial Design
4. Analysis of Covariance with Multiple Covariates
5. General Linear Hypothesis
6. General Linear Hypotheses with Contrasts
7. Multiple Range Tests

NON-REACTIVE CONSERVATIVE SPECIES

Using a seven-group scale suggested by Altshuller (14), based on hydrocarbon consumption, and used in the recent analysis of the 1968 field data by Eschenroeder and Martinez (12), the hydrocarbons found in the DOLA and Scott studies can be classified as in Table 1. Carbon monoxide (CO) is essentially non-reactive and is included in class 1. Other reactivity groupings have been suggested. The relative reactivity within the seven group scale, based on hydrocarbon consumption, is 0, 1, 3, 4, 8, 17 and 100 (15).

If we assume that both group 1 and 2 are non-reactive, we have some 30 equations to treat. Group 1 and 2 species do exhibit some reactivity (17, 18), but the relative amount compared to the higher groups should be small. Further, the most significant contribution to peak oxidant levels appears to be early morning source emissions (19), so that the inversion of the early hour balance is perhaps most important. Little reaction of the group 2 species would be expected in two to three hours. In practice some hydrocarbons species are missing in a large number of samples at DOLA and particularly at Huntington Park. In order to obtain a good set of statistical data, the number of hydrocarbon species in the analysis was limited to 24 for the DOLA data and 18 to 20 for the Scott data.

AUTOMOTIVE EXHAUST COMPOSITION

The validity and utility of the approach based on material balance depends, in part, on the representativeness of the compositional description of each source (the Q's in Equation 3). The selection of a proper set of coefficients for automotive exhaust is difficult as the composition varies considerably depending on the driving conditions and gasoline mix (6). Discrepancies between the ratio of hydrocarbons or acetylene to nitric oxide as measured according to the cycle and as measured in the atmosphere have been

noted (8). Simulation runs by Eschenroeder and Martinez were greatly improved when the ratio of acetylene to nitric oxide was increased from a value characteristic of the driving cycle, i.e. 0.2, to a value more indicative of atmospheric levels, i.e., 0.8. (3)

Data were collected by the California Air Resources Board in a vehicular tunnel during November, 1970 (20). The objectives of the study were to collect freshly-emitted exhaust samples representative of the total automobile and gasoline mix in the Los Angeles Basis. It was assumed that tunnel samples would provide a convenient and concentrated source of such samples. These data were provided by EPA, as part of the inputs to this program as a possible source of exhaust composition data. Our analysis which is presented below, indicated that these data are not representative of exhaust, and show evidence of considerable atmospheric dilution even in the tunnel.

The collection of representative compositional data for automobile exhaust and for full-spectrum gasoline proved to be a major and incompleted effort in the project. Detailed data were not found. A self-consistent method to generate appropriate composition parameters was developed, and is described more fully below.

GASOLINE COMPOSITION

The composition of gasoline used in the basin will determine the composition of spillage losses and vehicle evaporative losses. Assuming complete volatilization of spillage, the atmospheric concentration will reflect the gasoline full spectrum composition directly. In the initial analyses a composition reported by Maynard and Sanders for a typical premium gasoline was used (21). Premium gasoline represents about 75% of sales in the L.A. basin (20,22). Maynard and Sanders report data on a regular grade as well (21). Trying to typify the detailed composition of average Basin mix gasoline was an extremely difficult task. Data were obtained on average mix composition

based on Reid Vapor Pressure (RVP) or on overall proportions of saturates, olefins and aromatics (22), but not in terms of detailed hydrocarbon structure. Ultimately the search for actual composition data was abandoned in favor of a selfconsistent approach developed below. This represents a serious shortcoming in the present work, but can be avoided in the future by gathering samples of gasoline simultaneously with the atmospheric sampling program.. A considerable effort was made to obtain detailed hydrocarbon data from individual oil companies servicing the region, the American Petroleum Institute and several agencies.

EVAPORATIVE LOSS COMPOSITION

Initially the evaporative loss composition was calculated using a modified batch distillation approach, similar to that developed by a number of workers, for example, by Koehl (10). The exact composition is a function of temperature, degree of fullness of gasoline tank and other variables. The composition, according to Koehl's work, does not change greatly in the operating range that appears typical in the Los Angeles Basin. As above, this approach was also dropped in favor of the self-consistent technique.

NATURAL GAS COMPOSITION

It was believed that the major source of natural gas components in the atmosphere would result from seepage from the gas fields beneath the Basin, rather than from leakage in the distribution system supplying gas to the area, which gas contains a portion piped in from outside the Basin area. The natural gas composition used in the inversion computations is shown in Table 2 (23).

TABLE 2.

COMPOSITION OF NATURAL GAS

Species	Mol Percent
CH_4	81.1%
C_2H_6	9.7
C_3H_8	3.5
$i\text{-}C_4H_{10}$	0.19
$n\text{-}C_4H_{10}$	0.24
Inert	5.3

SECTION V

DEVELOPMENT OF SELF CONSISTENT COEFFICIENTS FOR GASOLINE BASED SOURCES

The failure to obtain detailed, directly-measured data on gasoline and exhaust composition was a major obstacle encountered in the study. Such data are absolutely essential to the whole analytic approach. As noted above a considerable effort was expended in a search for such data but was finally abandoned in favor of an indirect method, which, although limited in terms of the original anticipations, would, however, provide a basis for applying the material balance technique. The 1970 tunnel data which had been expected to provide a realistic estimate for exhaust composition, also provided disappointing results as noted by the following analysis.

Perusal of certain compounds in the 1970 tunnel series indicated that the tunnel data do not provide a reasonable measure of auto exhaust. The ratio of i-pentane to n-pentane in the tunnel averages about 1.3, whereas the ratio in the atmospheric data are clustered about a value of almost 2. The differential can be partially accounted for by the higher relative volatility of i-pentane, but not nearly sufficiently to explain the large discrepancy. Other discrepancies were also noted. It is possible that changes in the average gasoline composition over the two years between the 1968 and 1970 tests were responsible for the apparent mismatch.

An analysis was made to determine if the apparent inconsistencies were substantially due to the dilution of exhaust in the tunnel by outside ambient air. It was assumed the atmosphere in the tunnel contains not only auto exhaust but also some amount of outside atmosphere, in the ratio of exhaust-bearing tunnel air to outside air, 'P'. Values of P can be estimated from ratios of tunnel concentrations to atmosphere concentrations of individual hydrocarbon components. Inconsistent values were found for P in this way. For example, the very low methane level in the tunnel implied that very little outside air was drawn into the tunnel, i.e., P should be large. But, on the other hand, the ratio of n-pentane to acetylene in the tunnel is not much different from that in the atmosphere indicating that the tunnel sample was not very different from the atmosphere (i.e., P should be considerably less than one).

After trying several values, it was found that the value of 0.5 for P gave reasonable values for exhaust composition coefficients. Such a set of coefficients was used to invert the material balances for a sample set of days. The results of this inversion showed a considerably poorer fit for the sample days than that of the set of self-consistent coefficients as developed below. This adds weight to our conclusion that the tunnel data are not a realistic base for estimating the composition of automobile exhaust.

The failure of those data to provide a base for the exhaust coefficients produced a series of problems in finding a representative set as noted above. No single detailed gasoline composition reported in the literature seems representative, nor do the exhaust compositions reported by several authors (6, 24, 25).

A set of coefficients can be derived from the atmospheric data, per se, by making certain assumptions, first, that the atmospheric data can be typified by some mean set of parameters. The calculational procedure begins by taking the ratio of each conservative species to acetylene (assumed to be derived only from exhaust).

Starting with the basic material balance (Equation 8), we include only exhaust, evaporation and spillage, as:

$$C = \left[5.72 \times 10^{-5} R'_x e_x\right] + R'_v e_v + R'_s e_s \qquad (9)$$

Now, divide both sides by the equation for acetylene (Equation 10), (only the exhaust term exists) to obtain Equation 11.

$$C_a = 5.72 \times 10^{-5} R'_x e_a \qquad (10)$$

$$\frac{C}{C_a} = \frac{e_x}{e_a} + \frac{R'_v e_v}{5.72 \times 10^{-5} R'_x e_a} + \frac{R'_s e_s}{5.72 \times 10^{-5} R'_x e_a} \qquad (11)$$

A number of papers show that C_5 and higher paraffins appear in the exhaust in more or less constant proportion to their concentration in the gasoline (6, 24). Further, the concentration in the vaporized part (assuming a simple equilibrium distillation model) is related to the concentration in the whole gasoline through the volatility (10). These relationships can be expressed by the following two equations:

$$e_x = k_1 e_x \qquad (12)$$

$$e_v = k\, e_s \qquad (13)$$

where k_1 = proportionality contract relating exhaust composition to gasoline compositions

k = volatility

Substituting Equation 12 and 13 into Equation 11 and rearranging we get:

$$e_a\left(\frac{C}{C_a}\right) = \frac{e_x}{5.72 \times 10^{-5}}\left[5.72 \times 10^{-5} + \frac{R_v k_1 k}{R_x} + \frac{R_s k_1}{R_x}\right] \qquad (14)$$

Values of k_1 and k were obtained from the references indicated above (10, 24). Now if the acetylene content of the exhaust, the ratio of gasoline burned (R_v/R_x), and the ratio of gasoline spilled to gasoline burned (R_s/R_x) are known (on the average), the unknown, e_x, e_s, e_v can be determined

Spillage losses arise from liquid spill during transfer of gasoline to an automobile tank and from residual dripping from the filling nozzle. A report by Scott Research Laboratories on refueling losses provides a basis for estimating R_s/R_x. By combining data on liquid spill and nozzle drip losses from that study the amount of gasoline spilled is 0.3% or R_s/R_x equals 0.003.

About 6% of the gasoline burned ends up as hydrocarbons in the exhaust. Workers at the Bureau of Mines have shown that evaporative and exhaust contributions are of comparable magnitudes at ambient temperature above 60°F (26). That study indicates that exhaust and evaporative losses at an ambient temperature of 70°F are in the ratio 7/3, so that the percent of gasoline evaporated is about 2.7%, or R_v/R_x equals 0.027.

All that remains, then is to obtain an estimate of the average acetylene content of exhaust. Several approaches were used to arrive at that figure. One is based on measurements of carbon monoxide.

The CO content of exhaust is assumed to be 2.73% (by volume) of the total exhaust. That value was reported by G. W. Dickinson, et.al., (27) from a 500 car emission survey in L. A. in 1968 and corresponds reasonably to other survey data on samples considered representative of the automobile population in L. A. Multiplying that value by the mean of the ratio of acetylene of CO for all the samples taken at DOLA, the mean acetylene content of exhaust is 222 ppm. This value, which was used to obtain the coefficients appears to be consistent with levels measured by others or inferred from their measurements (24, 25, 27).

With these values and the mean ratio of each component to acetylene, a self-consistent set of "e's" can be derived. The resultant values are reported in the next section with the discussion of the inversion data.

SECTION VI

RESULTS OF MATERIAL BALANCE INVERSION

COMPUTER PROCEDURES

The material balance equations were inverted for each set of DOLA samples, which consisted of hourly samples at 5-6 a.m., 6-7 a.m., 7-8 a.m., 8-9 a.m., 10-11 a.m., 11-12 a.m., 1-2 p.m., and 2-3 p.m. Weekday samples were taken Tuesday through Friday. Weekend samples were taken on Sunday, but did not include the first and last hour periods. Input to the computer was a set of measured concentrations of the conservative species. Twenty-five compounds including carbon monoxide (CO), were considered to be non-reactive. These compounds are listed in Table 3, with the numerical code used in the computer analysis. Also input was a set of stoichiometric coefficients, calculated by the self-consistent method. The set used in the DOLA runs is given in Table 4. The output from the multiple regression and program contains the values for the six apparent source strengths, and a variety of statistical quantities representing the closeness of the fit to the observations. In terms of the notation in the computer output, as shown in Figure 1, each component is given as:

$$C_j = A + 5.72 \times 10^{-5} E_{9,j}R'_9 + E_{10,j}R'_{10} + E_{11,j}R'_{11} + 6.25E_{12,j}R'_{12}$$

$$+ 6.25E_{13,j}R'_{13} + 3.125E_{14,j}R'_{14} \qquad (15)$$

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TABLE 3.

LIST OF COMPOUNDS USED IN DOLA ANALYSIS

COMPOUND CODE	COMPOUND NAME
2	Ethane
4	Propane
5	Acetylene
6	Isobutane
7	n-butane
11	Isopentane
16	n-pentane
22	Cyclopentane/2-methylpentane
23	3-methylpentane
25	Hexane
27	2,2-Dimethylpentane
28	2,4-Dimethylpentane
34	3,3-Dimethylpentane
32	Cyclohexane
33	2-Methylhexane
34	2-3 Dimethylpentane
35	3-methylhexane
36	1-cis-3 Dimethylcyclopentane
37	2,2,4-Trimethylpentane
38	n-Heptane
39	Methylcyclohexane
41	n-Nonane
47	n-Decane
57	Methane
58	Carbon Monoxide

TABLE 4

STOICHIOMETRIC COEFFICIENTS*

USED IN THE

DOLA INVERSION RUNS

Compound No.	Exhaust	Evaporation	Spillage	Natural Gas	Methane	Propane
2	28.3			.097		
4		.0029	.0002	.0350		1.0
5	222.					
6	7.8	.0597	.0092	.0019		
7	43.5	.281	.0596	.0024		
11	60.4	.194	.0944			
16	32.0	.0806	.0500			
22	37.4	.0437	.0585			
23	17.6	.0186	.0275			
25	23.9	.0212	.0374			
27	1.3	.0008	.0020			
28	22.5	.0134	.0351			
31	.34	.0001	.0005			
32	4.3	.0025	.0067			
33	9.9	.0004	.0155			
34	6.3	.0027	.0098			
35	12.3	.0049	.019			
36	6.1	.0024	.0095			
37	18.9	.0058	.0295			
38	19.6	.0062	.0305			
39	17.0	.0049	.0265			
41	11.9	.0005	.0186			
47	19.7	.0003	.0308			
57	250.0			.811	1.0	
58	27300.					

* Exhaust coefficients in ppm (volume) others in mole fraction

SELECTION NO. 6= 4

SAMPLE SIZE 24
NO. OF VARIABLES 7 NO. OF VARIABLES DELETED 7 (FOR VARIABLES DELETED, SEE BELOW)
DEPENDENT VARIABLE IS NOW NO. 4

COEFFICIENT OF DETERMINATION 1.0000
MULTIPLE CORR. COEFFICIENT 1.0000

SUM OF SQUARES ATTRIBUTABLE TO REGRESSION 10334087.13440
SUM OF SQUARES OF DEVIATION FROM REGRESSION 59.09494

VARIANCE OF ESTIMATE 3.47617
STD. ERROR OF ESTIMATE 1.86445

INTERCEPT (A VALUE) -.19871

ANALYSIS OF VARIANCE FOR THE MULTIPLE LINEAR REGRESSION

SOURCE OF VARIATION	D.F.	SUM OF SQUARES	MEAN SQUARES	F VALUE
DUE TO REGRESSION.....	6	10334087.13440	1722347.855734954	72.4479
DEVIATION ABOUT REGRESSION...	17	59.09494	3.47617	
TOTAL...	23	10334146.22933		

VARIABLE NO.	MEAN	STD. DEVIATION	REG. COEFF.	STD.ERROR OF REG.COE.	COMPUTED T VALUE	PARTIAL CORR. COE.	SUM OF SQ. ADDED	PROP. VAR. CUM.
9	.00208	.00392	3540.02924	157.61719	22.45906	.98356	5434215.454R1	.53069
10	.03126	.16747	172.90665	8.54180	20.24241	.97988	10[illegible]544.39651	.01050
11	.02378	.12370	54.09088	25.48644	2.10344	.65444	80483.58285	.00774
12	.24869	1.03519	170.21560	3.27736	51.93673	.99686	4585420.45794	.44372
13	.26062	1.27574	381.84735	2.66108	143.50834	.99959	75421.79145	.00730
14	.13021	.03789	.33854	.65388	.51768	.12387	.92082	.00000
4	155.35943	670.30043						

COMP. CHECK ON FINAL COEFF. .33854

VARIABLES DELETED... 5 6 7 8 1 2 3

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Figure 1. Computer Output

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where A = intercept of the multiple regression equation
E = stoichiometric coefficient
R' = apparent source strength
Subscripts 9, 10, 11, 12, 13, 14 = exhaust, spillage, evaporation, natural gas, methane and propane respectively.

The apparent source strengths appear in Figure 1, under the column labeled (Reg)ression (Coeff)icients. In the example shown, the exhaust apparent source strength is 3540. The intercept is shown as the A value, here equal to -0.19871. An estimate of the standard error between the measured concentration and the predicted value is given. The value in this case was 1.864 ppb, which means on the average, the material balances will estimate the concentration of each species to within ±1.86 ppb. A second part of the output for each run, is a list of predicted concentrations, shown in Table 5. The compounds are listed in the same order as shown in Table 3. Note that methane (observation number 24) and propane (observation number 2) are fit exactly, in accordance with the inclusion of special sources for these two compounds. The example shown here does not include CO. Duplicate runs including CO were made for most samples. The only formal difference would be the addition of another line to the table of residuals (Table 5). As noted below, the summaries of the individual runs were made on the runs <u>without</u> CO.

GENERAL RESULTS

In some runs, negative values of source strength for evaporation (and in a few cases for spillage) were found. This represents a physically impossible case and indicates that:

1. The method is inapplicable and the linear material balances do not represent the atmosphere, or

TABLE 5.

TABLE OF RESIDUALS

OBSERVATION	Y VALUE	Y ESTIMATE	RESIDUAL
1	106.75000	106.72935	.02065
2	38.00000	38.00000	.00000
3	44.80000	44.75966	.04034
4	16.40000	14.24017	2.15983
5	60.47000	63.01375	-2.54375
6	51.92000	50.71827	1.20173
7	28.44000	22.94886	5.49114
8	16.02000	18.13064	-2.11064
9	8.77000	8.09596	.67404
10	10.75000	10.38107	.36893
11	.46000	.29674	.16326
12	9.10000	8.60348	.49652
13	.33000	-.08329	.41329
14	1.74000	1.44479	.29521
15	3.38000	3.37798	.00202
16	2.61000	2.07823	.53177
17	4.14000	4.16511	-.02511
18	1.29000	1.97456	-.71456
19	4.24000	6.23988	-2.14988
20	5.66000	6.50530	-.84530
21	4.07000	5.53056	-1.46056
22	2.77000	3.31166	-.54166
23	4.05000	5.53495	-1.48695
24	3300.00000	3300.00000	-.00000

TEST OF EXTREME RESIDUALS

RATIO OF RANGES FOR THE SMALLEST RESIDUAL..... .116
RATIO OF RANGES FOR THE LARGEST RESIDUAL..... .564

CRITICAL VALUE OF THE RATIO AT ALPHA = .10 ... .367

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2. The natural inherent uncertainty in the measurements and the input parameters can result formally in an apparent physical paradox. This will be seen most in the smallest source as a consequence of the best-fit algorithm, or

3. The actual reaction and disappearance of some of the paraffins, which are assumed to be conserved in the analysis, lead to negative values.

We believe that the latter two explanations for the observed results, not the first, are more likely the basis. The fit, using the self-consistent set of coefficients is, in general, quite good. The 24 individual hydrocarbon species are fit on the average to a few ppb over concentrations ranging from almost zero to several hundred ppb.

The most significant influence on the results of the material balance inversion procedure is the wide spread encountered in the input data. Of the 25 so-called non-reactive compounds including CO, all but three are generally present in the atmosphere at levels of under 100 ppb. Ethane, however, usually appears somewhere between 100 and 200 ppb and CO and methane are usually measured at around 3000 ppb or higher. Since the inversion procedure uses a least-square linear regression analysis to fit these data, it tends to give undue weight to fitting those data points which are furthest from the mean values. As a result, these three compounds (methane, ethane, and CO) can be expected to dominate the fit. In the case of methane, the addition of an independent source of methane frees this compound from influencing the regression fit. Thus, with methane free, ethane and CO (CO in particular) become the dominant compounds in fitting the data.

This excessive weighting of two compounds is very significant. In the case of CO, the result is that, since CO appears in auto exhaust alone, the exhaust component will be fit almost entirely by the measured CO levels; other exhaust components will have negligible effect on the exhaust fit. In the case of ethane, a similar process happens with respect to the natural gas source. With methane floating, the fit for this source is dominated by the ethane levels.

Now with the exhaust and natural gas fit determined, there will exist a fixed residual level for all remaining compounds:

$$r_i = c_i - \varepsilon_{i,9}R_9 - \varepsilon_{i,12}R_{12} \qquad (16)$$

where r_i is the residual level of compound i (ppb)
c_i is the measured concentration of compound i (ppb)
$\varepsilon_{i,9}R_9$, $\varepsilon_{i,12}R_{12}$ are the source composition and source strength coefficients for exhaust and natural gas, respectively.

These residual levels represent the set of data against which gasoline evaporation and gasoline spillage sources are fit. Since no particular compounds dominate the fit to this set of data, the evaporation and spillage sources are estimated using the information available in the entire set of residual data.

The importance of this understanding of the regression procedure is that it points out the sensitivity of this model to choices of source composition coefficients. If CO is included, the precision and accuracy of the exhaust prediction is directly equivalent to that of the CO source coefficient, while the precision and accuracy of the natural gas prediction is almost equivalent to that of the ethane source coefficient. Precision of the spillage and evaporation prediction, however, are more complex. These predictions are based on source coefficients for all hydrocarbon species as well as on the

residuals. Since these residuals in turn are based on the exhaust and natural gas predictions, it follows that the accuracy of prediction of spillage and evaporation sources is limited by the accuracy of the CO and ethane coefficients. Additional lack of precision results from the imprecision in the other hydrocarbon coefficients.

As an alternative procedure, CO can be omitted so that the exhaust is fitted more by the hydrocarbon components. In this case, the next most dominant species, acetylene, will have the largest effect, but far less than CO. This should improve the overall method. The results presented hereunder were obtained with CO excluded. From the runs with CO included it was noted that the computed regression coefficients (source strengths) were comparable, indicating that the CO/acetylene ratio used to characterize exhaust composition is probably quite realistic.

Inversion of the Scott data from Huntington Park was considerably more difficult than that for the DOLA data. Grab samples were taken at random times so that no consistent temporal patterns could be developed. Samples for the light hydrocarbons (C_2 - C_4) were taken separately and at different times than those for the heavier hydrocarbons (C_5 - C_{10}). Attempts were made to associate contemporary or almost contemporary samples in the inversion procedure. The results were disappointing. The data showed considerable scatter and appearance of negative source strengths. As a result, only the DOLA data have been completely analyzed, and are discussed in the sections below.

APPARENT SOURCE STRENGTH RESULTS

The results of the inversion computations for the DOLA data are displayed in Figures 2 through 7. The averaged values for week days and weekends are shown as functions of time of day. There were 28 weekdays and 10 weekend (Sunday) samples. The samples were taken at 0530, 0630, 0730, 0830, 1030, 1130, 1330 and 1430 on weekdays. On Sundays, the first

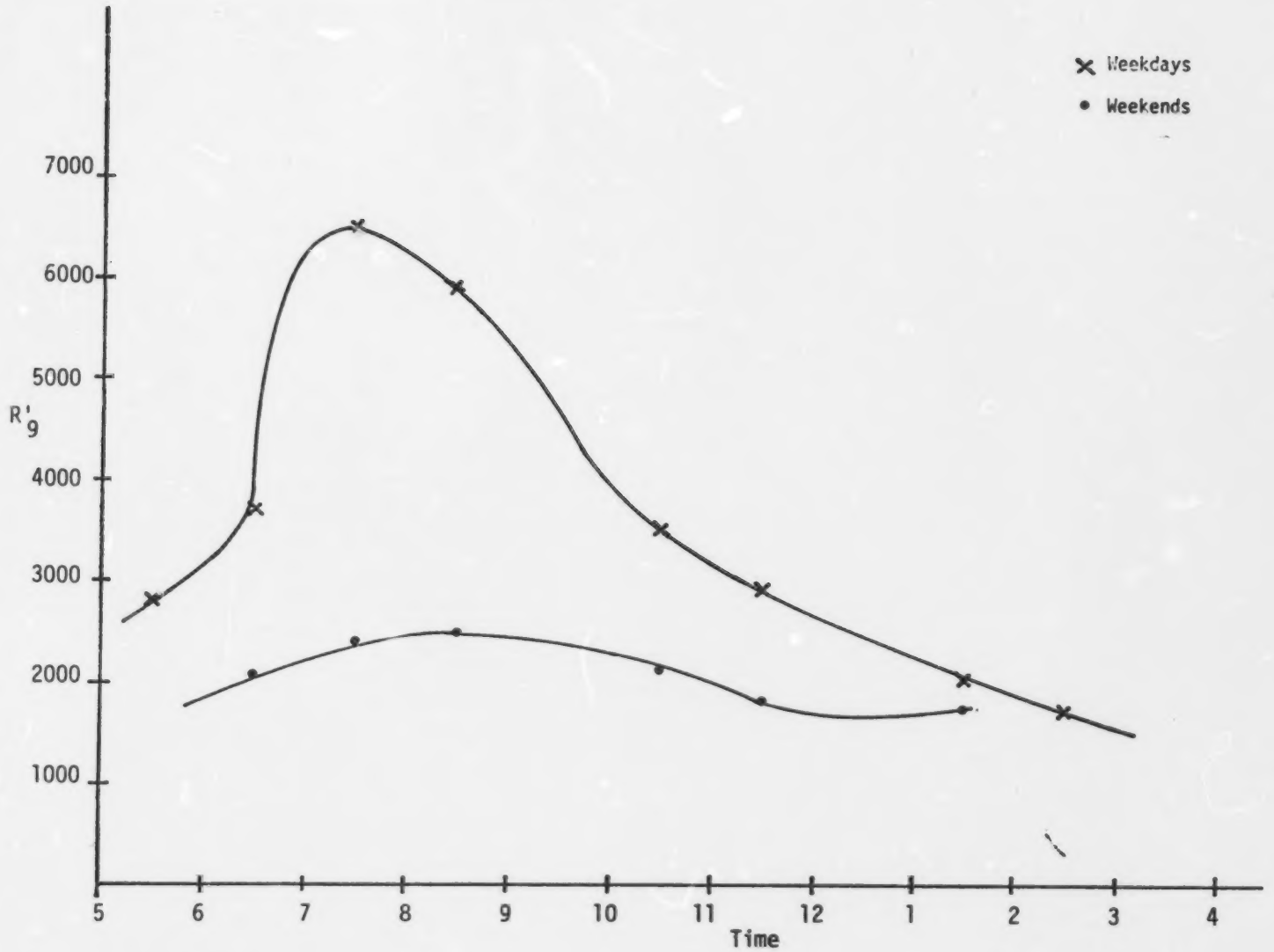

Figure 2. Apparent Source Strength-Exhaust

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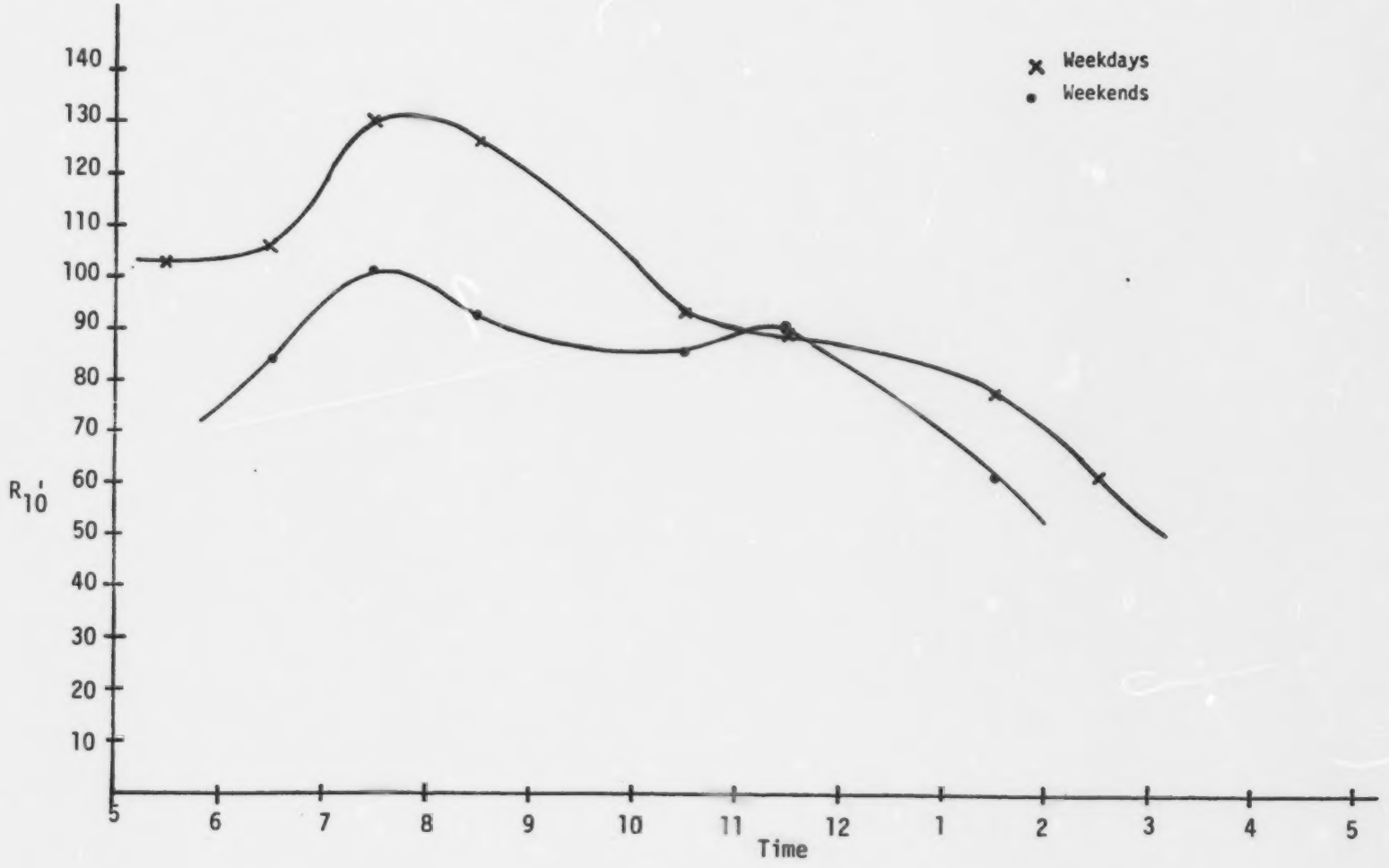

Figure 3. Apparent Source Strength-Spillage

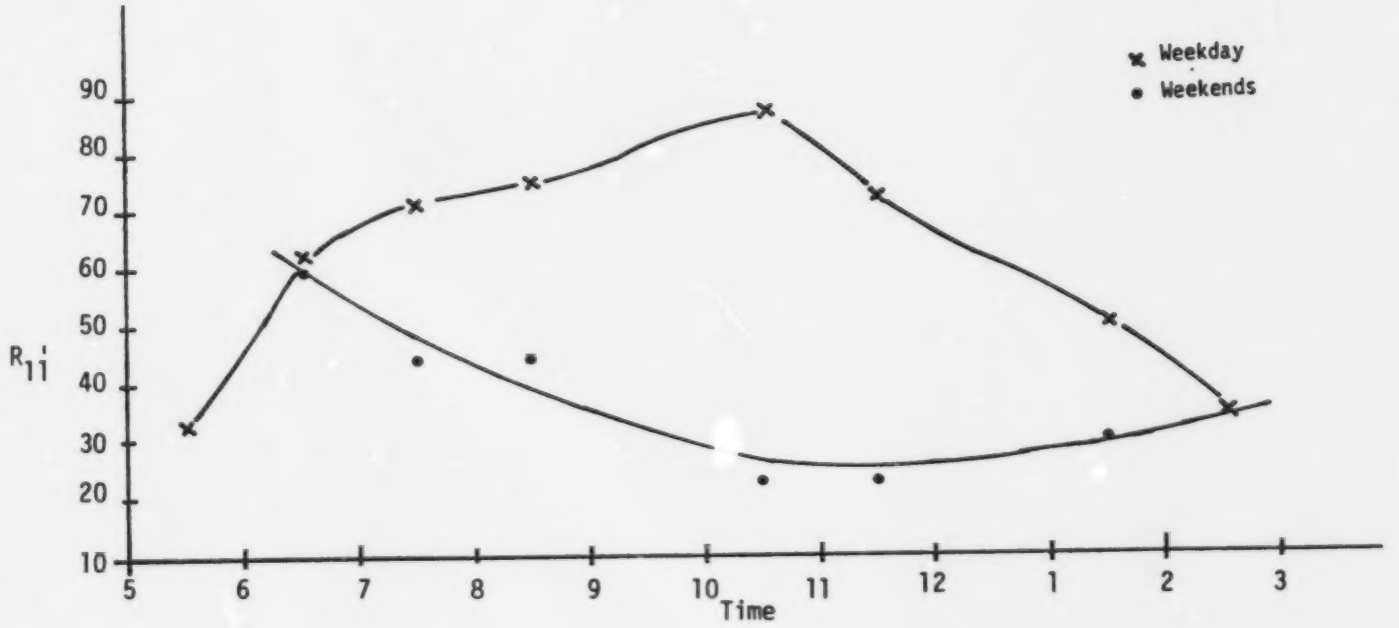

Figure 4. Apparent Source Strength-Evaporation

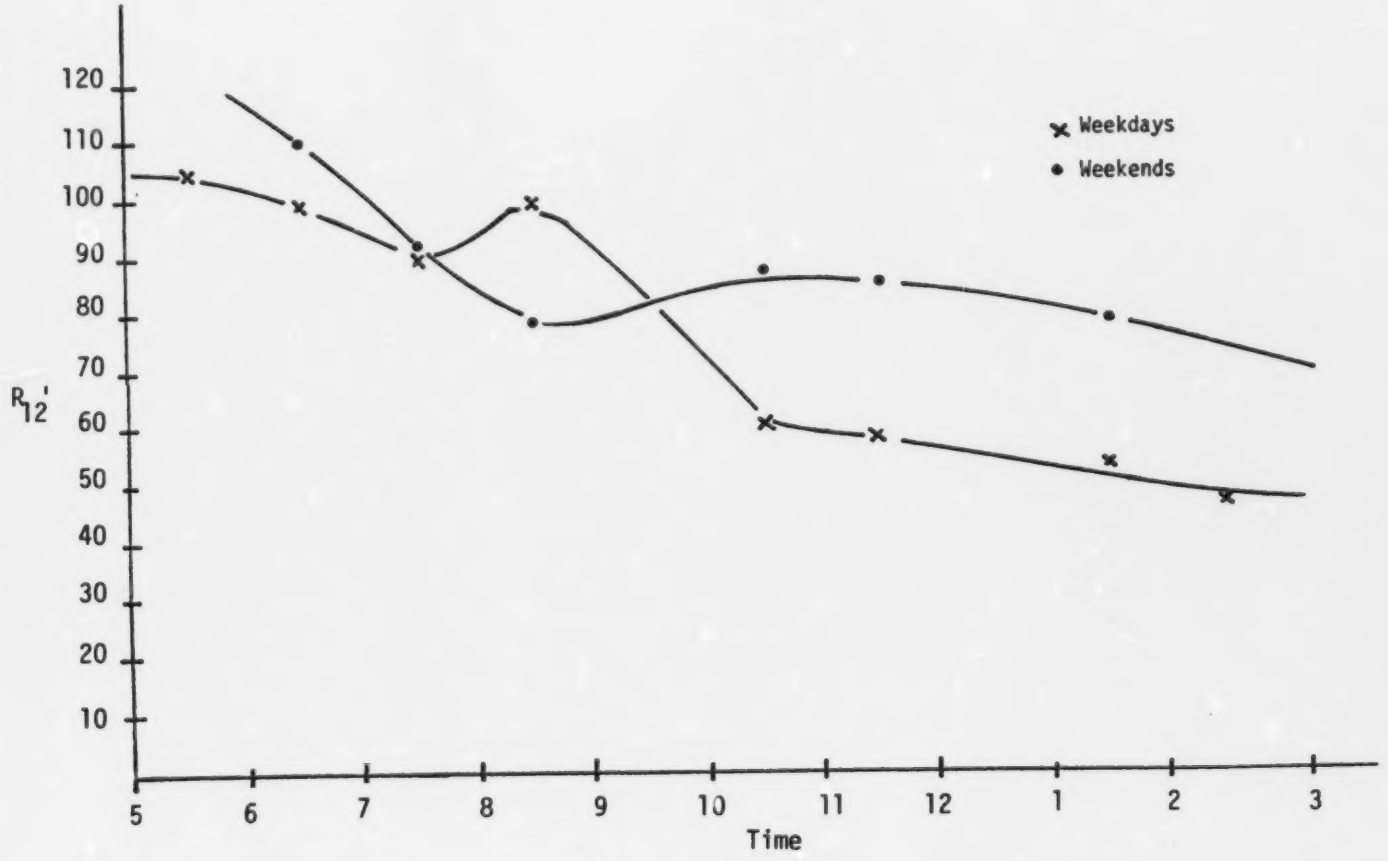

Figure 5. Apparent Source Strength-Natural Gas

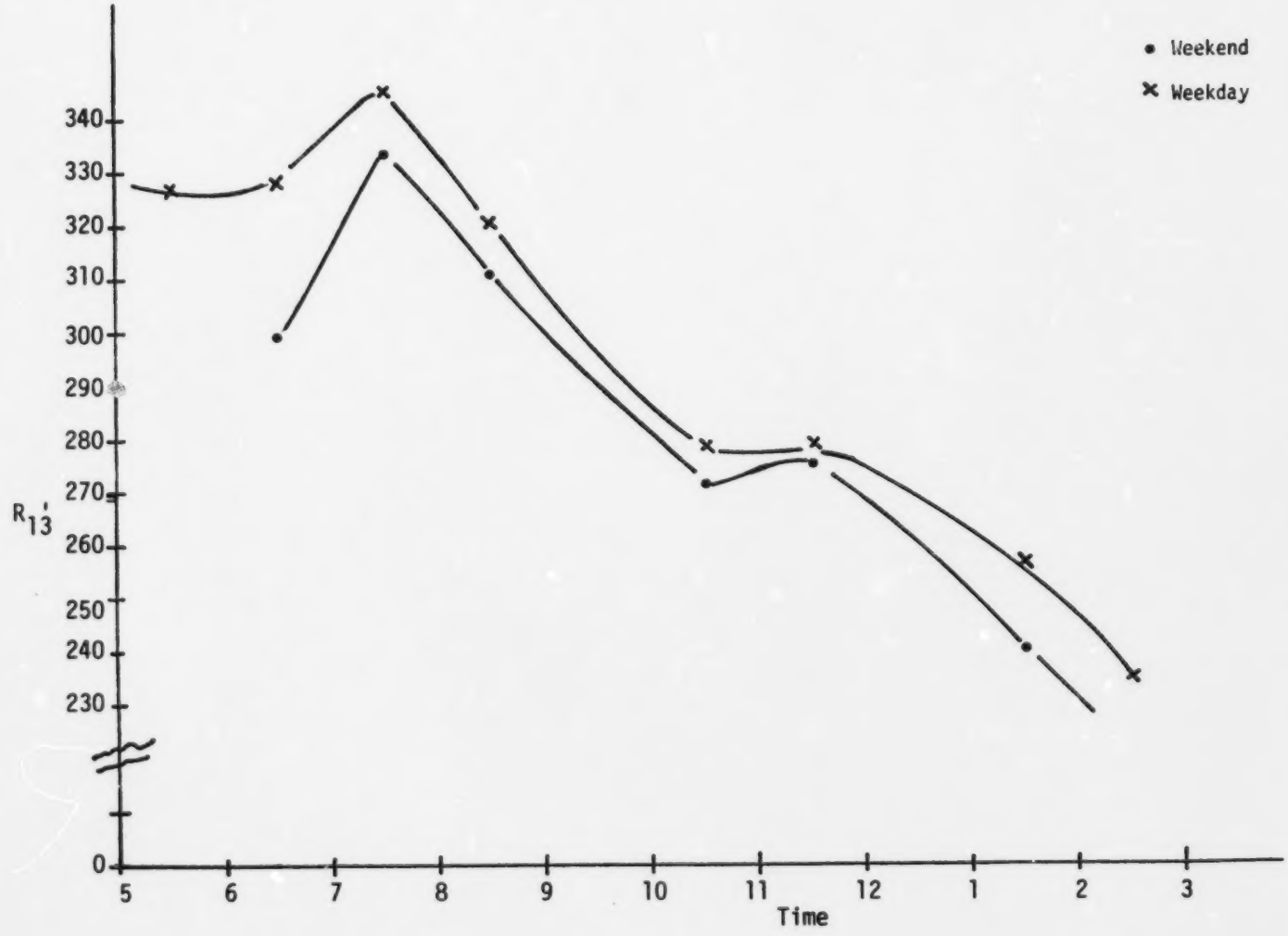

Figure 6. Apparent Source Strength-Methane

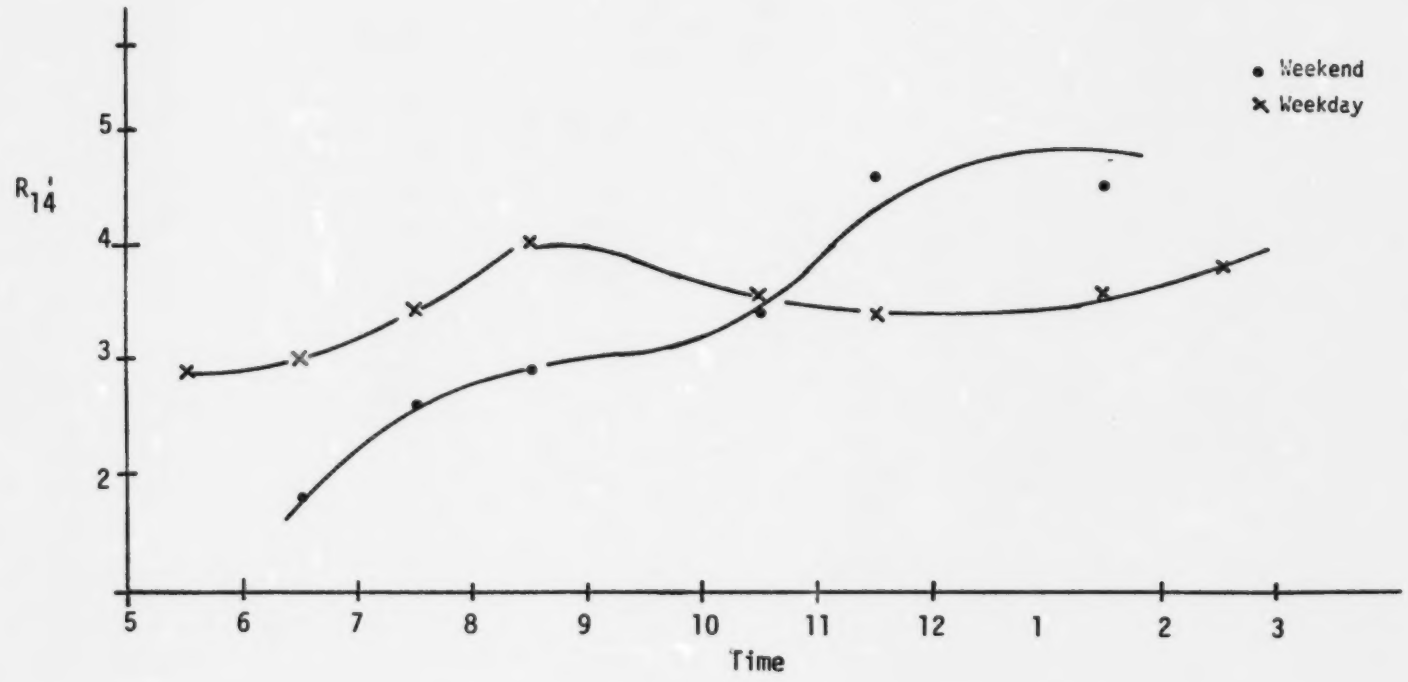

Figure 7. Apparent Source Strength-Propane

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and the last samples were omitted. The individual apparent source strength values are quite scattered about the mean. The coefficient of variations, i.e., standard deviations divided by the mean, runs between 50% and 100% for the gasoline-derived sources, with the highest degree of scatter in the morning samples. The unknown methane source (R'_{13}) showed surprising little scatter compared to the other sources.

If we assume that the basic emission sources, such as automobile density or natural-gas leakage, do not change significantly from day to day, then the variability in the apparent strength may be largely attributed to atmospheric variability from hour-to-hour and day-to-day. In particular the inversion layer, that so typically limits mixing in the early morning, lifts during the day, allowing upward diffusion and a consequent apparent reduction in source strength. Note that the actual strength should be proportional to mixing height.

Examination of these curves shows, clearly, a larger exhaust emission on weekdays, as would be expected. Spillage and evaporative emissions appear to be somewhat larger on weekdays, but not greatly so. Natural gas and the methane and propane sources do not show any significant differences between days and weekends. The striking similarity in the weekday and weekend curves for the unknown methane source (R'_{13}), and the consistently lower scatter suggests a natural source. The equivalent concentration of methane corresponding to the source is obtained by multiplying R'_{13} by 6.25 (as shown in Equation 15) and ranges from about 2000 ppb in the early morning to about 1500 ppb in the afternoon. These values correspond to the range of methane in the global background, and it seems reasonable to hypothesize that this source represents the methane present in the air entering the basin.

The downward trend during the day may be due to the replacement of the initial (early morning) air mass which may have been largely composed of parcels having terrestrial origin and consequently, the higher methane background, by parcels of marine origin with lower methane content. If this hypotheses is correct, then the large variation in observed levels of methane could be due to the trapping of natural gas in the basin under widely-varying mixing characteristics.

NORMALIZED SOURCE STRENGTHS

Although the average source strength curves displayed above appear to show diurnal patterns that seem reasonable, there remains, as noted, considerable scatter in the data. It is possible to reduce the scatter in the data by referring the apparent source strengths (R') to the apparent source strength for natural gas. If one assumes that the rate of emission of natural gas into the atmosphere in the basin is constant, unaffected by diurnal or daily cycles, then variations in the apparent values, R', as computed, should be the result of atmospheric variability. The effect of that variability should be removed or least reduced by dividing the apparent source strengths for exhaust, evaporative and spillage by the corresponding natural gas value, prior to computing the averages.

The results of such a normalization procedure are displayed in Figures 8 through 10, showing the diurnal patterns for normalized source strength, S. The degree of scatter is markedly reduced as shown in the following set of data (Table 6) from two separate Sundays. As shown, the derived exhaust strengths were almost an order of magnitude apart but were reduced to approximately equal values after normalization. The atmospheric concentrations of hydrocarbons observed on those two days were also almost an order of magnitude apart. The weekend to weekday differences also become more apparent. The coefficient of variation ranges from 20-50%, considerably less than in the corresponding apparent source strengths.

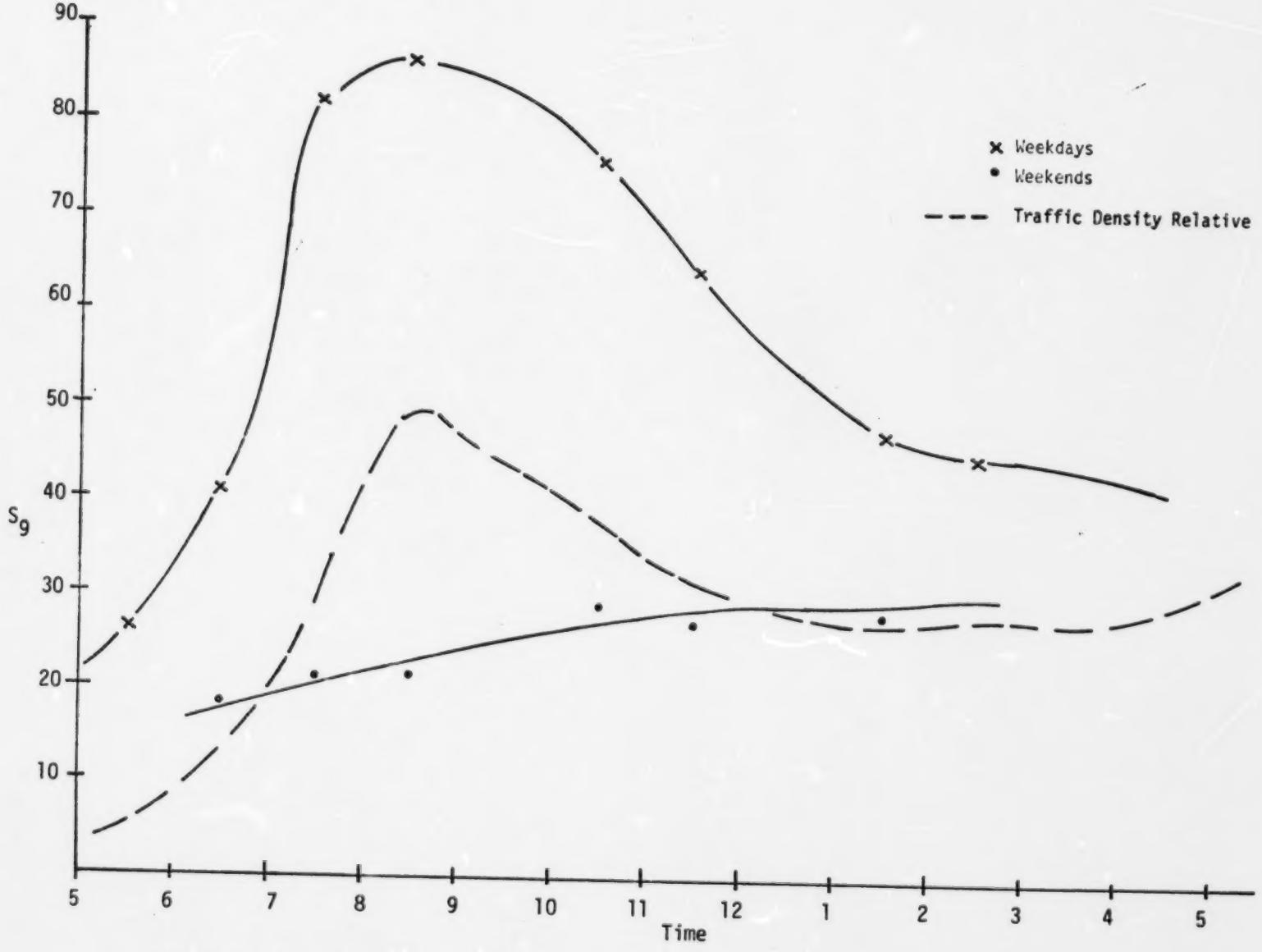

Figure 8. Normalized Source Strength-Exhaust

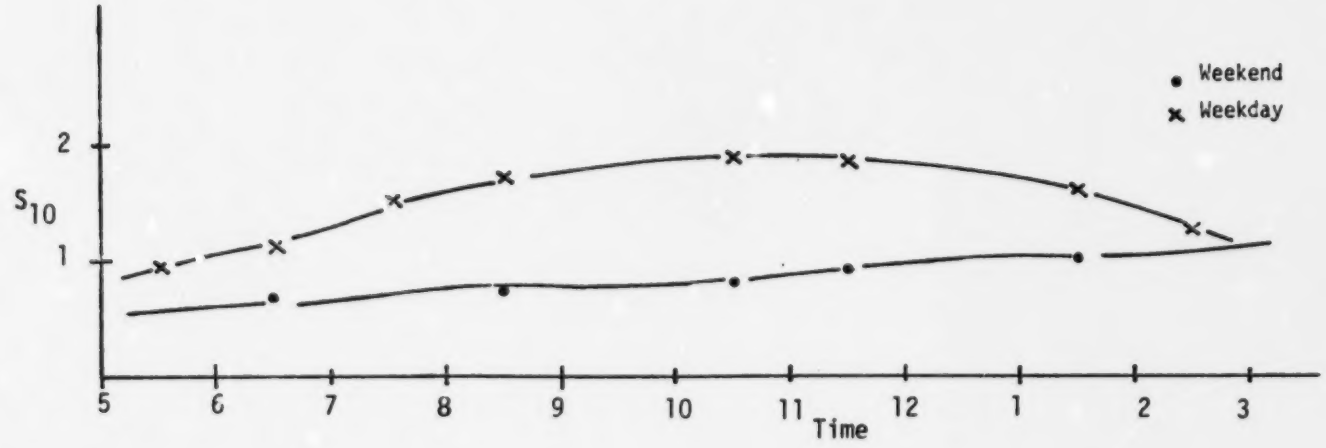

Figure 9. Normalized Source Strength-Spillage

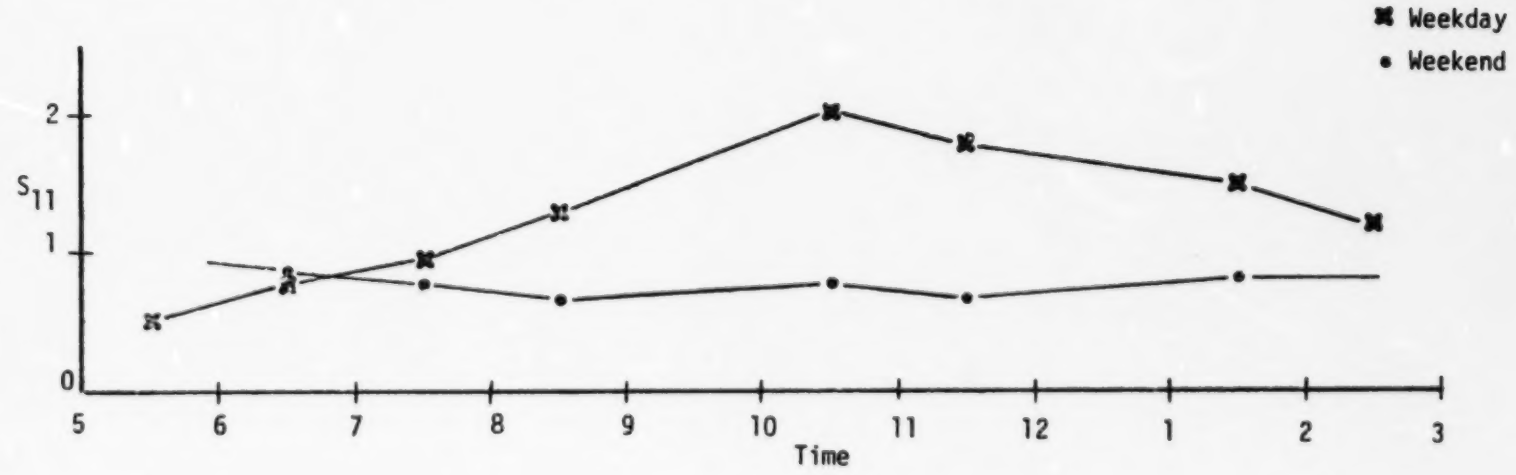

Figure 10. Normalized Source Strength-Evaporation

TABLE 6.

A. UNNORMALIZED EXHAUST SOURCE STRENGTHS

	6-7	7-8	8-9	10-11	11-12	1-2
Sunday 9/29	358	403	422	479	479	---
Sunday 10/27	---	4920	5600	5810	4000	2535

B. NORMALIZED SOURCE STRENGTHS

	6-7	7-8	8-9	10-11	11-12	1-2
Sunday 9/29	16	21	20	26	18	---
Sunday 10/27	---	19	20	25	15	30

The value of the normalized source strength is a measure of the quantity of gasoline emitted through the three proposed routes, exhaust, spillage and evaporation. As noted earlier, some of the values for evaporation or occasionally spillage regression coefficients were negative. Thus, the separate quantities are subject to considerable uncertainty. The sum of the two showed less scatter, and has been plotted in Figure 11. The peak in the evaporative and spillage curve appears later in the day than does the peak of the exhaust curve. This may be due to the generation of emissions by carburetor hot soak, after the cars have been parked in the morning, and also may follow the general heating during the morning.

Superimposed in Figure 8 is a curve for the weekday traffic density pattern typical of Los Angeles freeway traffic (28). The general shape of the source strength curve fits *a priori* expectations. The early morning buildup follows automotive traffic density growth. Since the source strength represents the integrated source contributions to the air parcel samples, the magnitude of this quantity should remain more or less constant at the peak value until advection and inversion lifting begin to clear out the stagnant air during mid-morning hours. For most of the days sampled, a sharp decrease in unnormalized source strength was found to occur in the mid-morning period, which behavior pattern would appear to be due to air movement.

The values of the normalized source strength are proportional to the mass of fuel consumed in the three separate emission modes. The relative contributions of each of the three gasoline-derived modes to atmospheric non-methane hydrocarbon are shown in Figures 12 to 15. As above a graph of the combined contribution of evaporation and spillage is included. The same data are presented in a cumulative percentage diagram in Figures 16 and 17, for the weekdays and weekend samples, respectively. The dominance of exhaust is during the week is evident in Figure 16 although the sum of evaporative and spillage losses appear more important in the weekend pattern.

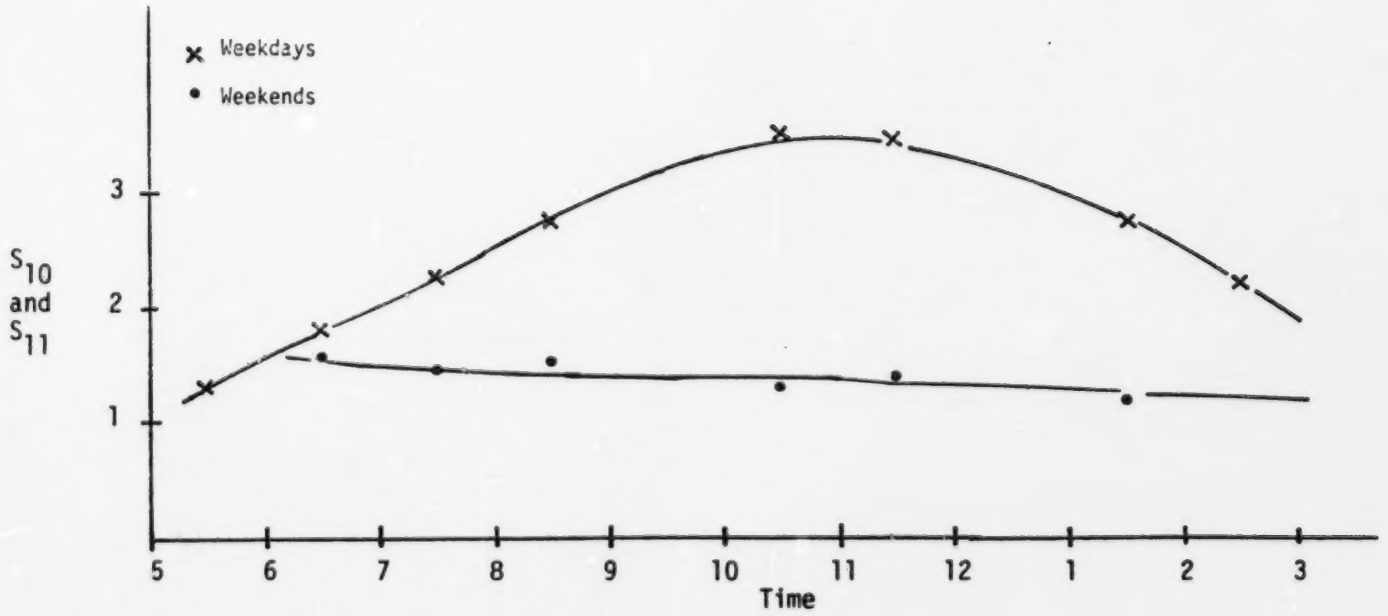

Figure 11. Normalized Source Strength - Combined Spillage and Evaporation

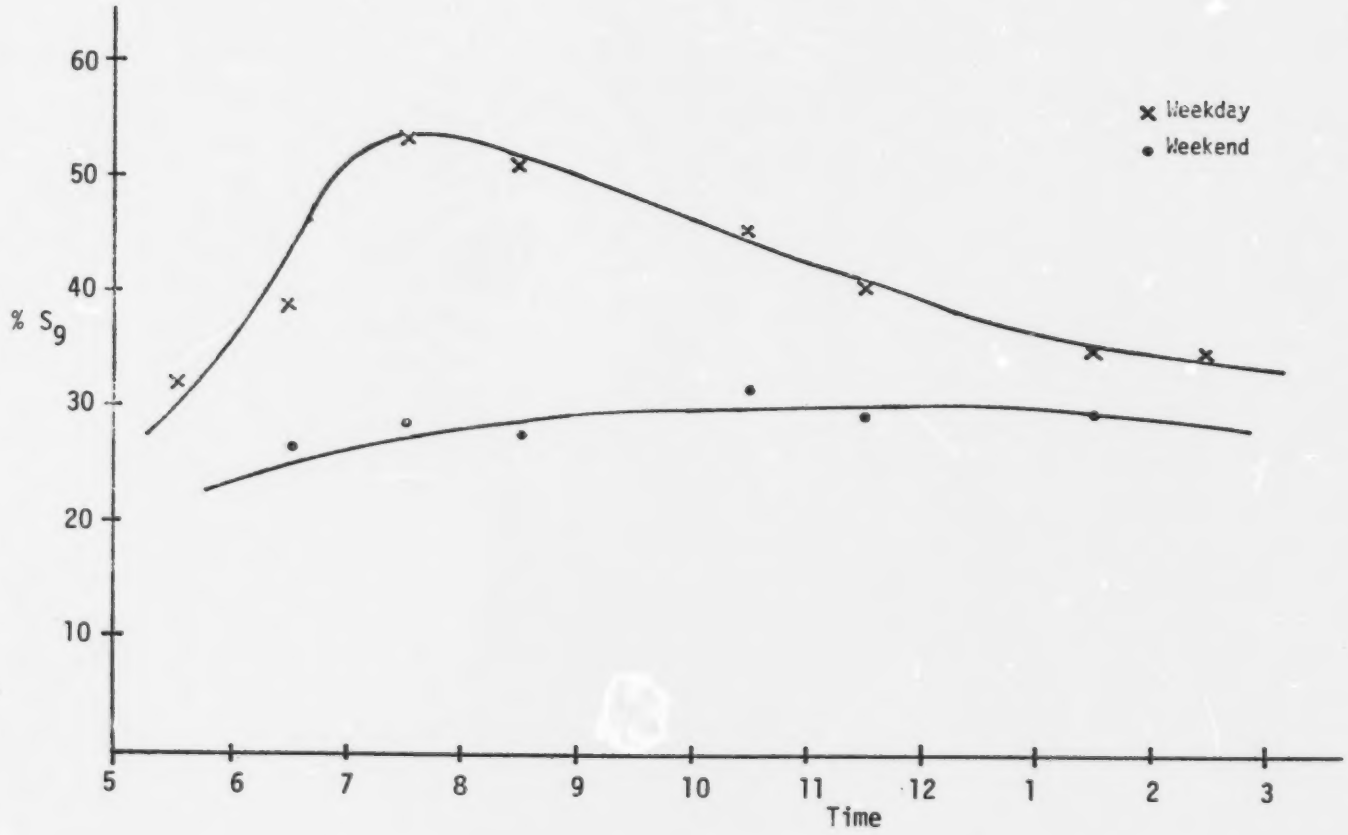

Figure 12. Relative Contribution To Non-Methane Hydrocarbons - Exhaust

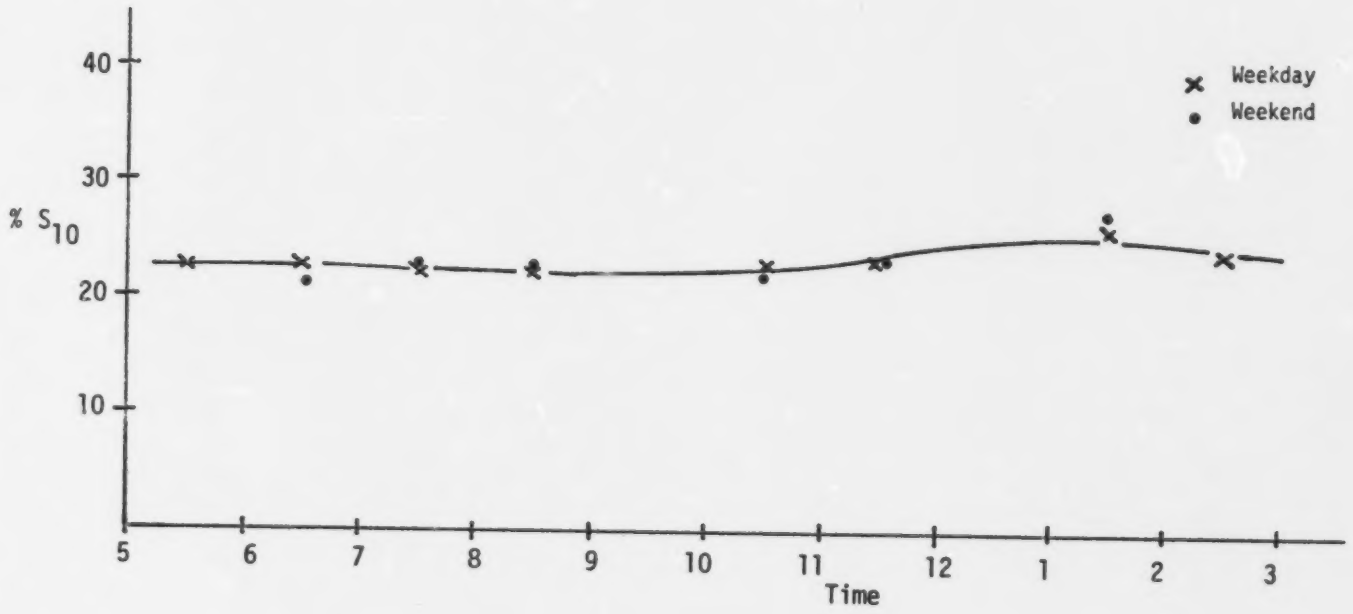

Figure 13. Spillage - Contribution to Non-Methane Hydrocarbon

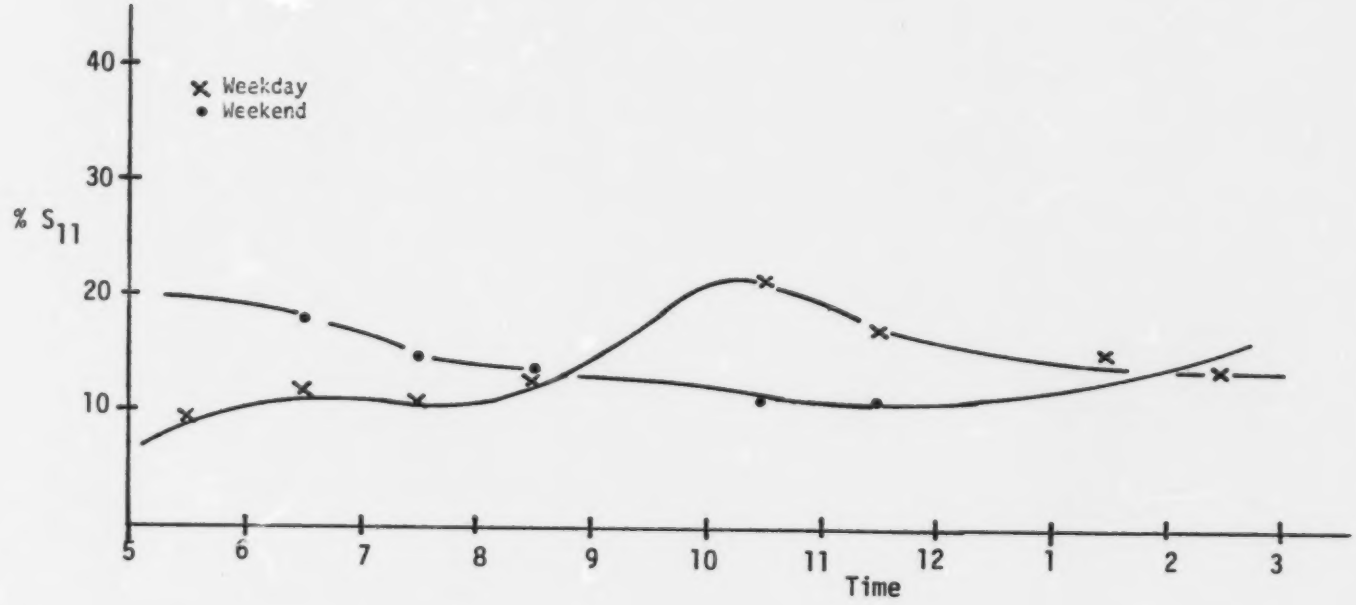

Figure 14. Evaporation Contribution to Non-Methane Hydrocarbons

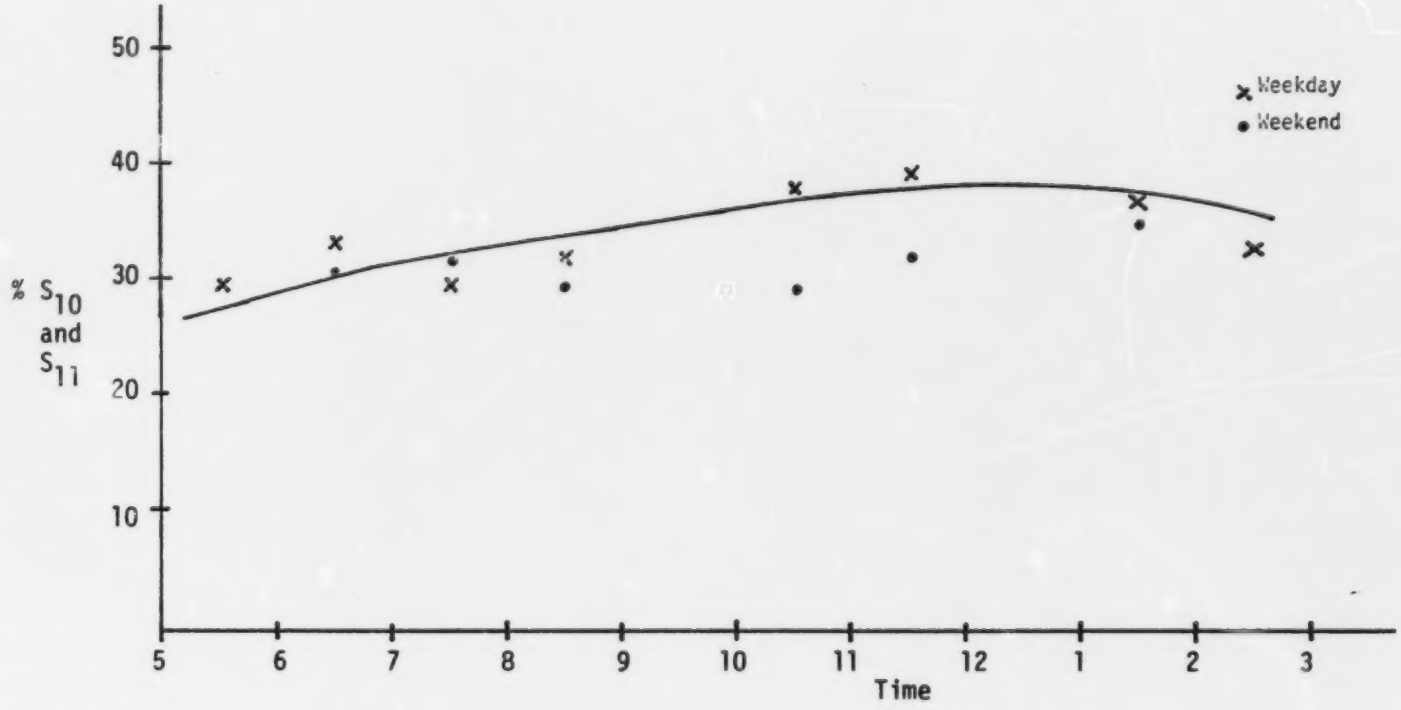

Figure 15. Combined Spillage and Evaporation - Contribution to Non-Methane Hydrocarbons

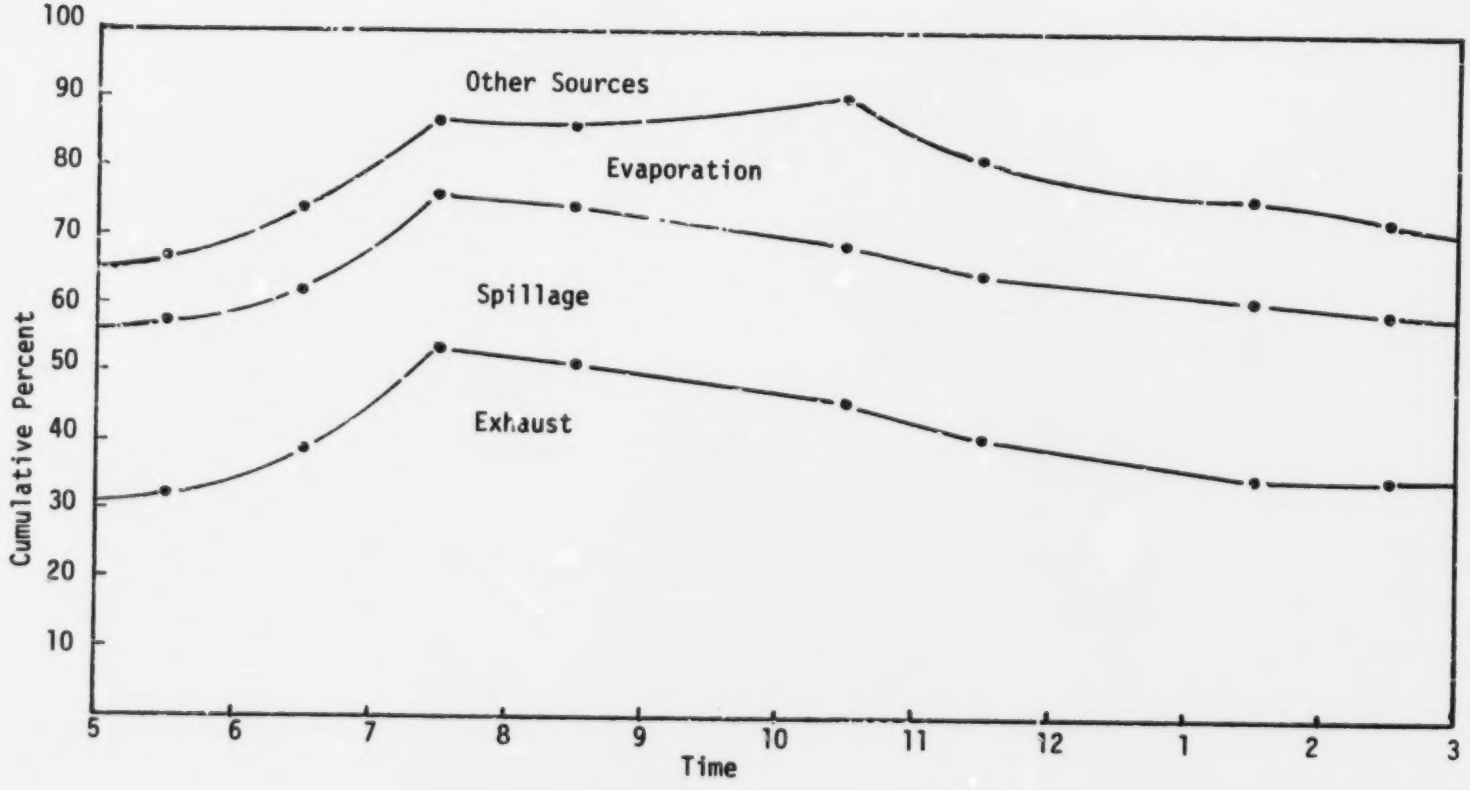

Figure 16. Components of Non-Methane Hydrocarbons - Weekdays

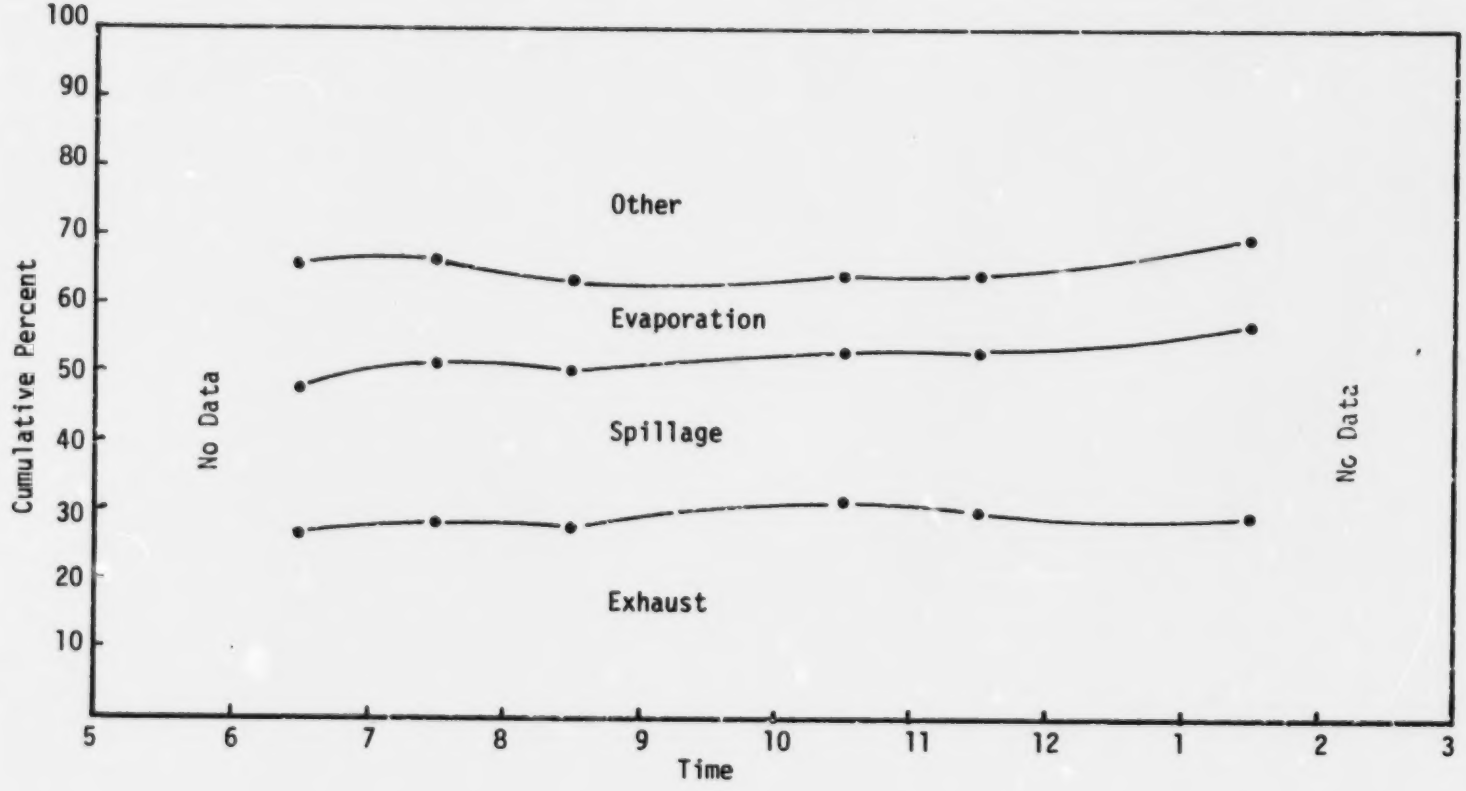

Figure 17. Components of Non-Methane Hydrocarbons - Weekends

If these results represent properly the different sources of atmospheric hydrocarbons, it follows that reducing evaporative and spillage losses is as important as reducing exhaust hydrocarbons.

It is possible to compare the estimate of source strength to other estimates of emissions. The actual source strength is related to the inversion regression value (R') by the relationship in Equation 7 above. Substituting appropriate values for p, T, R_g, the equation becomes:

$$R(kg/m^2) = 4.0 \times 10^{-9} R'L \qquad (17)$$

where L is the mixing height in meters. During the fall, the mixing height is less than 150 meters about half the time. The source strength of hydrocarbons from exhaust and evaporation at 0900 is about 350, assuming that about 5% of the hydrocarbons consumed in the vehicle appears in the exhaust. This number is equivalent to about 540 kilograms per square mile.

The traffic density in the area near the DOLA sampling site was estimated by Roberts, et.al., (28) to be approximately 200,000 vehicle-miles per square mile per day. In urban driving, an emission factor of about 8.3 grams per mile appears typical. Using this value and assuming conditions in 1968 were about the same, the daily emissions per square mile would be about 1660 kilograms per mile per day.

Based on freeway traffic measurements (see Figure 18) the early morning peak accounts for about 30% of the total traffic for the day (29), or about 500 kilograms per square mile of the total daily output. This value agrees with the estimate very closely, and lends credence to the whole approach.

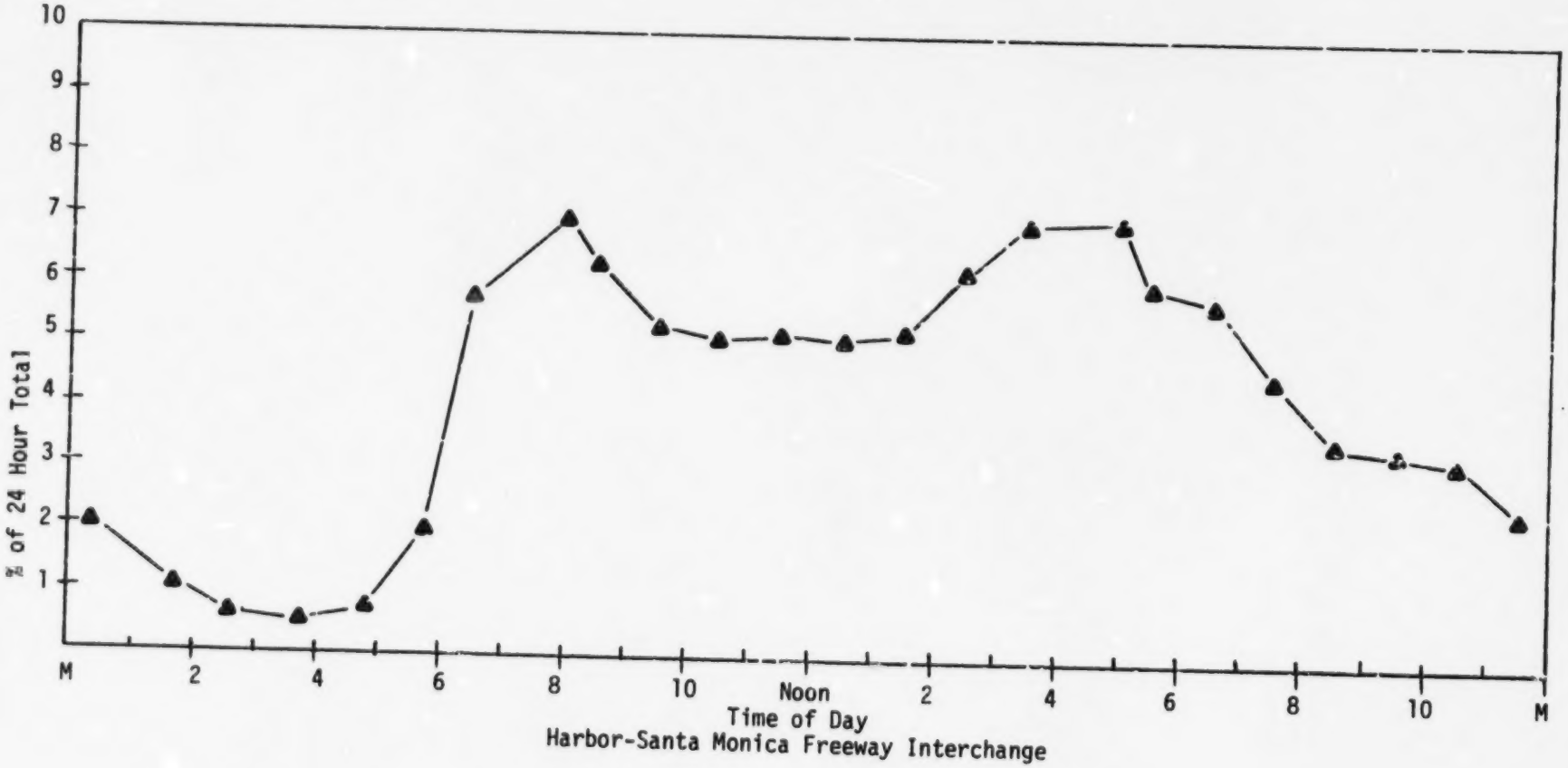

Figure 18. Traffic Versus Time of Day

LOSS OF REACTIVE COMPOUNDS

Having estimated source strengths by inverting the material balance equations for the non-reactive compounds, it is now possible to reverse the process for the reactive compounds and to use the computed source strengths to estimate their concentrations assuming that no reaction took place. The equation here is:

$$C'_j = \sum \varepsilon_{ij} R'_i \qquad (18)$$

where the R'_i's are the source strengths, ε_{ij}'s are the source composition coefficients, and C'_j is the predicted concentration of the j^{th} reactive compound assuming no reaction took place.

The difference between C'_j and the actual concentration measured for the j^{th} compound at that time is then an estimate of the amount of the j^{th} species that has reacted. This difference, as a percentage of C'_j is an unbiased estimate of the percent of compound j that has reacted for a given air parcel at a given time.

This procedure has been carried out for two of the reactive compounds (ethylene and propylene) on the sample set of days. Estimates of the two species in unreacted exhaust were drawn from the literature (6, 24). Figure 19 shows some typical daily patterns of percent propylene and percent ethylene reacted. The initial morning levels are not zero, and represent the accumulation of unreacted material in the air masses being sampled. As expected, the percent reacted shows a rise from very low levels in the morning to a peak that occurs usually after about 10:00 a.m. Since each daily cycle of measurements is made on the composition in a changing sample of air, it is expected that this curve will not always continue to rise with time. New emissions of unreacted material are accumulating at the same time that reaction is depleting the material. The percent reacted thus reflects a balance between additional emissions and continuing reactions. The peaks of those curves may indicate the point in the day when increasing auto emissions balance the depletion rate due to reaction.

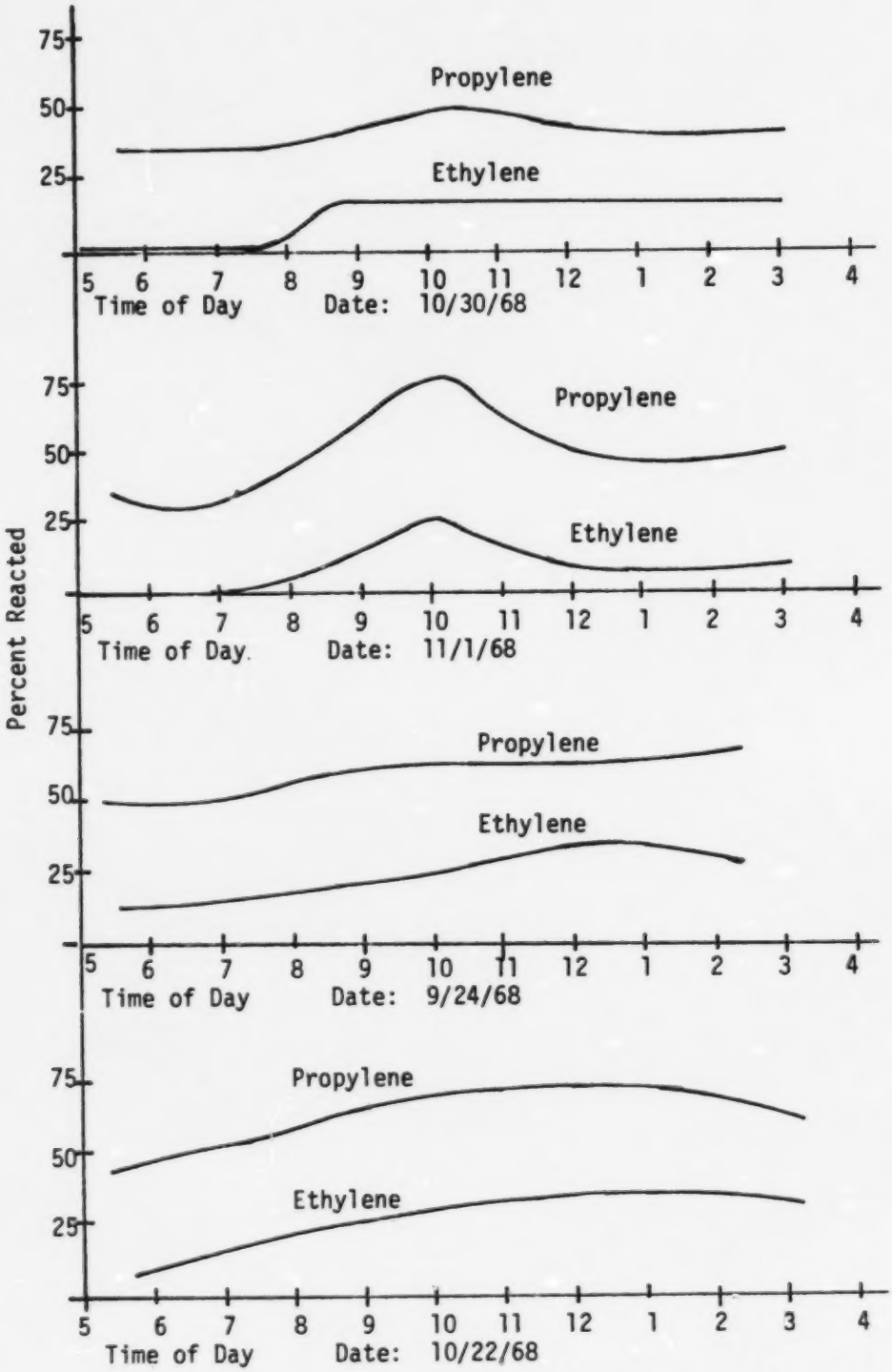

Figure 19. Percent Ethylene and Propylene Reacted on Individual Days

The average loss curves for the entire set of days are plotted in Figure 20. The curves appear to show a difference between weekday and weekend curves. The difference is not statistically significant. The propylene and ethylene loss data showed a remarkably low degree of scatter about the mean value. The coefficient of variation was generally below 25%. Since the basic data are much more highly scattered, the narrowness of the spread of the derived quantity supports the reasonableness of the approach. The difference in loss between the two species is of the same degree as is the reactivity as measured in the laboratory.

Unfortunately, we could not apply this technique to other reactive species. The lack of data on composition of exhaust and gasoline precluded reliable estimates of the stoichiometric coefficients of the higher molecular weight species. Ethylene and propylene are emitted essentially only in exhaust. Given reliable data on all of the reactive species, this technique appears to be capable of estimating the degree to which the compounds have been consumed.

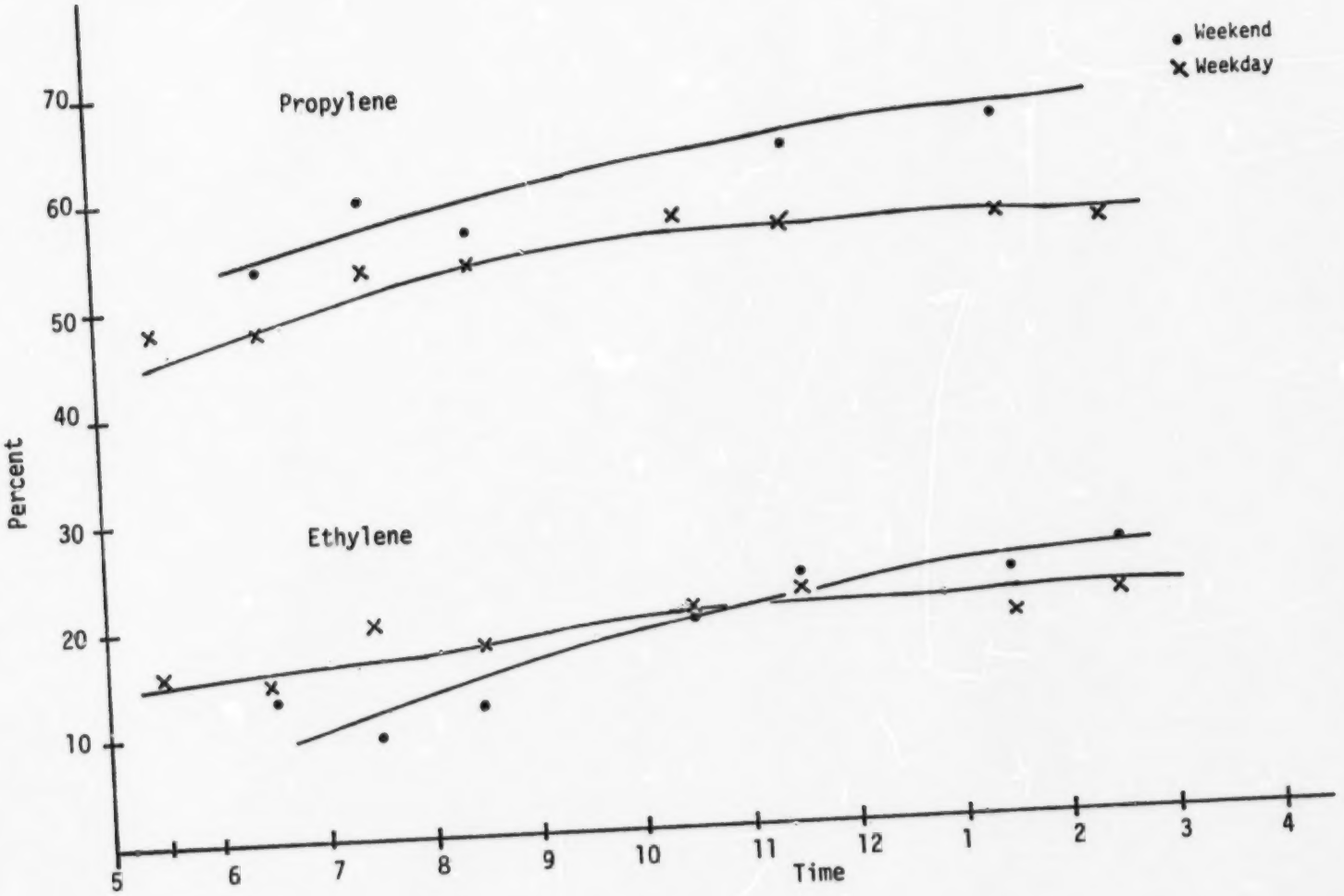

Figure 20. Averaged Percent Loss of Ethylene and Propylene

SECTION VII

DIRECT STATISTICAL ANALYSIS OF ATMOSPHERIC DATA

ANALYSIS OF VARIANCE OF ATMOSPHERIC DATA

An analysis of the variance in the atmospheric data was performed initially in order to classify these data prior to the inversion analysis. The aim of this classification was to reduce the variance in each set of data to be analyzed by dividing the daily observations into more or less homogeneous classes. Tentative hypotheses to be tested in the analysis were that:

1. The automotive exhaust, the gas spillage and the evaporation sources are about the same from weekday to weekday, but will show considerable weekend-to-weekday variation.

2. Within each day there is considerable hour-to-hour variation in the exhaust, spillage and evaporation sources.

3. The day-to-day variation in the natural gas source is insignificant but from hour-to-hour within a given day the variation may be significant.

These hypotheses were tested as follows, using an analysis of variance program in the BIOMED statistical package. The analysis of variance was carried out on the composition data without transformation. It was believed that the robust characteristics of the standard analysis of various methodology would provide valid answers on such a large set of data without transformation. On that base screening for normality was not done.

To examine auto exhaust emissions, CO was assumed to be the key compound. CO was classified first by day of the week (for weekdays only) and the within- and between-day variances were calculated. The results showed that there was no significant difference between days (weekday only) at 1% significance level test (see Table 7a).

The same CO data were then classified by weekday vs. weekend. In this case, there were three data groups - Tuesday, Wednesday, and Sunday observations. The day-to-day variance in this case was significant at the 1% significance level (see Table 7b).

The CO data were then classified by hour of day into eight groups. The hour-to-hour vairation was thus shown to be significant at the 1% significance level (see Table 7c).

To examine emissions from spillage and evaporation sources, i-pentane was selected as the key compound. A similar series of tests were run and the variance between weekdays was shown to be insiginficant at the 1% level. Weekday-to-weekend variance, as well as hour-to-hour variance within a given day were shown to be significant at the 1% level (see Tables 7d, 7e, and 7f).

To examine the natural gas emission source, methane was selected as the key compound. A similar series of tests were made and the weekday-to-weekday as well as weekday-to-weekend variance was shown to be insignificant at the 1% significance level. The variance in methane levels from hour-to-hour within a given day, however, was shown to be significant at the 1% level (see Table 7g, 7h, and 7i).

The main conclusions derived from this set of analyses are, first, that in the analysis of the automotive exhaust source, and of the spillage and evaporation sources, data should be broken into a two-way classification - hour-by-hour and weekday-by-weekend - in order to reduce the intrinsic variability in the data sets. In the case of the natural gas source, data need be classified only by time of day to reduce variability.

TABLE 7
ANALYSIS OF VARIANCE RESULTS

7a. Analysis of Variance on CO - among weekdays.

Source of variance	d.f.	Sum of Square	Mean Square
between days	4	116.7	29.2
within days	206	3169.8	15.4

$F_{4,206} = 1.9$

7b. Analysis of Variance on CO - weekday vs. weekend.

Source of Variance	d.f.	Sum of Square	Mean Square
between days	2	126.5	63.25
within days	168	1506.6	9.0

$F_{2,168} = 7.1$

7c. Analysis of Variance on CO - among hours.

Source of Variance	d.f.	Sum of Squares	Mean Square
between hours	7	1198.2	171.2
within hours	203	2088.2	10.3

$F_{7,203} = 16.6$

Walden

7d. Analysis of Variance on i-pentane - among weekdays.

Source of Variance	d.f.	Sum of Squares	Mean Square
between days	4	105286	26321
within days	213	2556268	12000

$F_{4,213} = 2.2$

7e. Analysis of Variance on i-pentane - weekday vs. weekend.

Source of Variance	d.f.	Sum of Squares	Mean Square
between days	2	80283	40142
within days	168	1432961	8530

$F_{2,168} = 4.7$

7f. Analysis of Variance on i-pentane - among hours

Source of Variance	d.f.	Sum of Squares	Mean Square
between hours	7	614140	87734
within hours	268	2676628	999

$F_{7,268} = 8.8$

7g. Analysis of variance on methane - among weekdays.

Source of Variance	d.f.	Sum of Squares	Mean Square
between days	4	4.3	1.07
within days	206	93.96	.46

$F_{4,206} = 2.36$

Walden

7h. Analysis of variance on methane - weekday vs. weekend

Source of Variance	d.f.	Sum of Squares	Mean Square
between days	2	.668	.33
within days	168	78.6	.47

$F_{2,168} = .71$

7i. Analysis of Variance on methane - among hours

Source of Variance	d.f.	Sum of Squares	Mean Squares
between hours	7	27.1	3.9
within hours	203	71.2	.35

$F_{7,203} = 11.04$

It was assumed that the weekday-to-weekend variability in exhaust, spillage and evaporation data was due to variability in source strengths while the hour-to-hour variability in these data was due to both source variations and diurnal meteorological patterns. The hour-to-hour variations in natural gas data were assumed to result only from diurnal meteorological patterns. Hour-to-hour variations in exhaust, spillage and evaporation source strengths can thus be amplified by taking the ratio of these source strengths to the natural gas source strength as discussed above.

Thus, the analysis of variance study was the basis of the treatment of the data in the inversion process. The difference in exhaust source strength from hour-to-hour and weekend-to-weekday was clearly evident as shown earlier. Other source components followed the patterns predicted according to the statistical analysis on the raw data set.

PAIRWISE CORRELATIONS

DOLA Data

The DOLA and Scott data were put through a multiple correlation analysis. The program used for the DOLA data was limited to a 20 x 20 matrix so that three overlapping runs were required to assemble the entire array. Incomplete records where any compound was missing were eliminated. Out of the 304 hour/day combinations existing, about 160 have complete records. By partitioning the whole set, larger samples could be included in the correlation analysis. For this number of samples, a significant correlation coefficient is about 0.70. Figure 21 shows the pairwise correlation matrix. The compound codes correspond to those used in the EPA coding scheme, and are noted in Table 8.

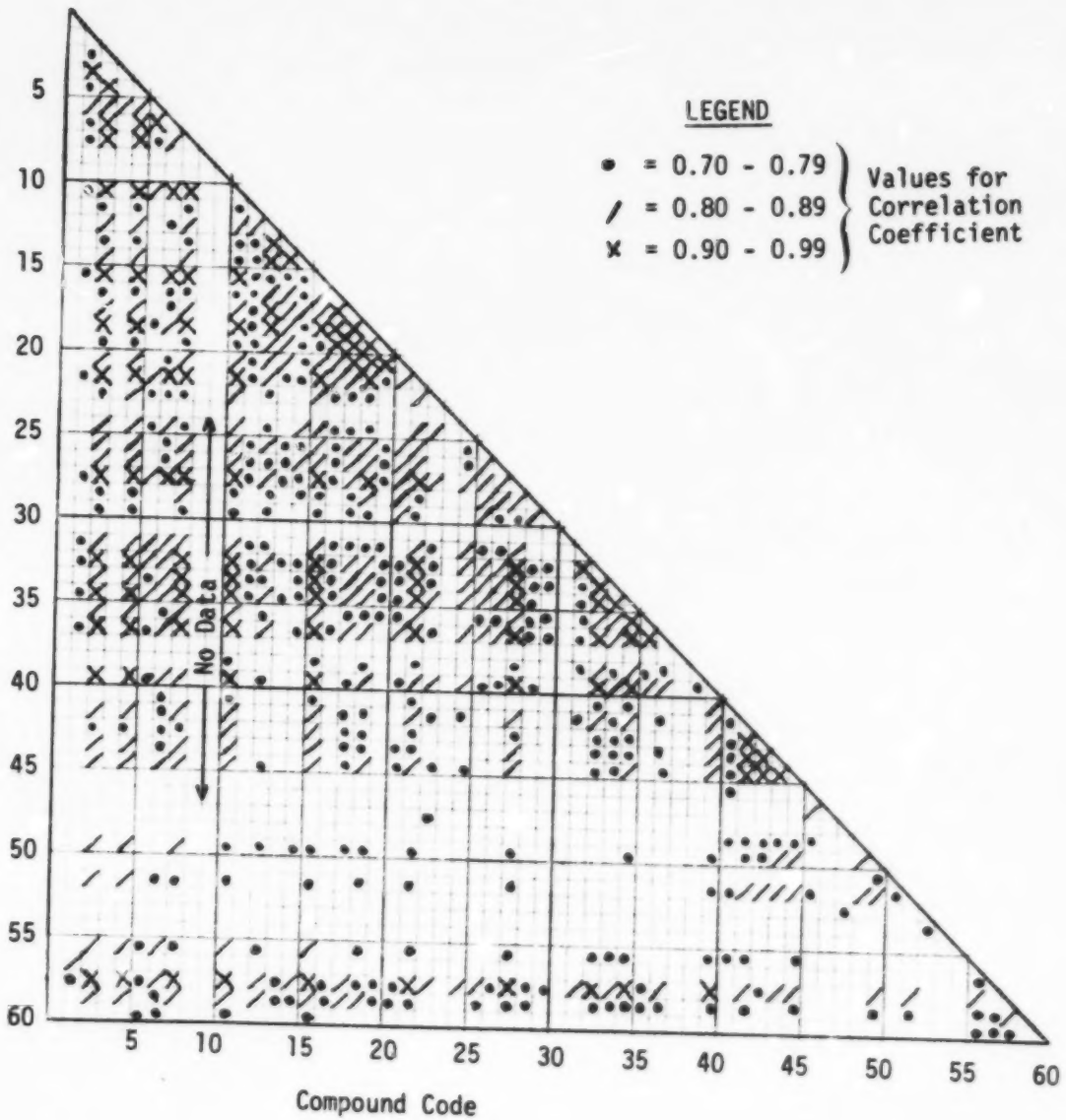

Figure 21. DOLA Data - Pairwise Correlation Coefficient Matrix

TABLE 8

CODES USED IN DATA COMPUTERIZATION
DOLA DATA

1. Not Used
2. Ethane
3. Ethylene
4. Propane
5. Acetylene
6. Isobutane
7. n-Butane
8. Propylene
9. Propadiene
10. Neopentane
11. Isopentane
12. 1-Butene + iso-Butylene
13. trans-Butene-2 + Methylacetylene
14. cis-Butene-2
15. Butadiene-1,3
16. n-Pentane
17. Pentene-1
18. 2-Methylbutene-1
19. trans-Pentene-2
20. cis-Pentene-2
21. 2-Methybutene-2
22. Cyclopentane + 2-Methylpentane
23. 3-Methylpentane
24. 4-Methylpentene-2
25. Hexane
26. Hexene-1
27. 2,2-Dimethylpentane
28. 2,4-Dimethylpentane
29. 2-Methylpentene
30. cis-2-Hexene
31. 3,3-Dimethylpentane
32. Cyclohexane
33. 2-Methylhexane
34. 2,3-Dimethylpentane
35. 3-Methylhexane
36. 1,cis,3-Dimethylcyclopentane
37. 2,2,4-Trimethylpentane
38. n-Heptane
39. Methylcyclohexane
40. Toluene
41. Nonane
42. Ethylbenzene
43. p-Xylene
44. m-Xylene
45. o-Xylene
46. Isopropylbenzene + Styrene
47. n-Decane
48. n-Propylbenzene
49. m+p-Ethyltoluene
50. 1,3,5-Trimethylbenzene
51. tert-Butylbenzene + o-Ethyltoluene
52. sec-Butylbenzene + 1,2,4-Trimethylbenzene
53. Unknown
54. 1,2,3-Trimethylbenzene
55. n-Butylbenzene + p-Diethylbenzene
56. Non-Methane HC (FIA)
57. Methane (FIA)
58. Carbon Monoxide
59. NO_x
60. NO_2

Walden

Some correlation was expected. The principal exhaust components CO and C_2H_2, are very highly correlated. The overall pattern can be attributed to common ancestrage for the compounds and to external factors such as temperature, stability, or mixing depth. At this point in the analysis, there was insufficient information to make the necessary distinction.

The apparent lack of correlation generally along the rows between 45-55 may be due to analytic problems. An examination of the raw data shows many zero values that do not seem consistent with nearby data. These zeros will reduce the apparent correlation. Propane (Compound No. 4) shows a correlation only with isobutane (Compound No. 6). This lack or correlation with gasoline or natural gas species supports the concept of a separate, as yet not understood, source of propane and explains the improvement in the inversion results after such a source was added.

Scott Data

The treatment of the Scott data required a much larger effort in the preparative stages, and a special program was written to match up data on the various parameters, taken at somewhat different times. Atmospheric quantities (such as temperature and humidity) and non-hydrocarbon pollutants (CO, oxidants, total hydrocarbons) were reported as hour or half-hour averages. Light hydrocarbons (C_1 - C_4) were sampled separately from the heavier fractions (C_5 - C_{10}). A simple pairwise correlation routine was included in the data preparation program. The results are presented in Figure 22. Atmospheric parameters have been included as well as the individual hydrocarbon species. The identification code for the variables is given in Table 9.

The results agree generally with those for the DOLA data set. CO and acetylene are well correlated with other exhaust gas hydrocarbons. It is interesting to note that nitrogen dioxide is not correlated with any other variable, but nitric oxide is, on the other hand, correlated (although weakly) with many of the exhaust components.

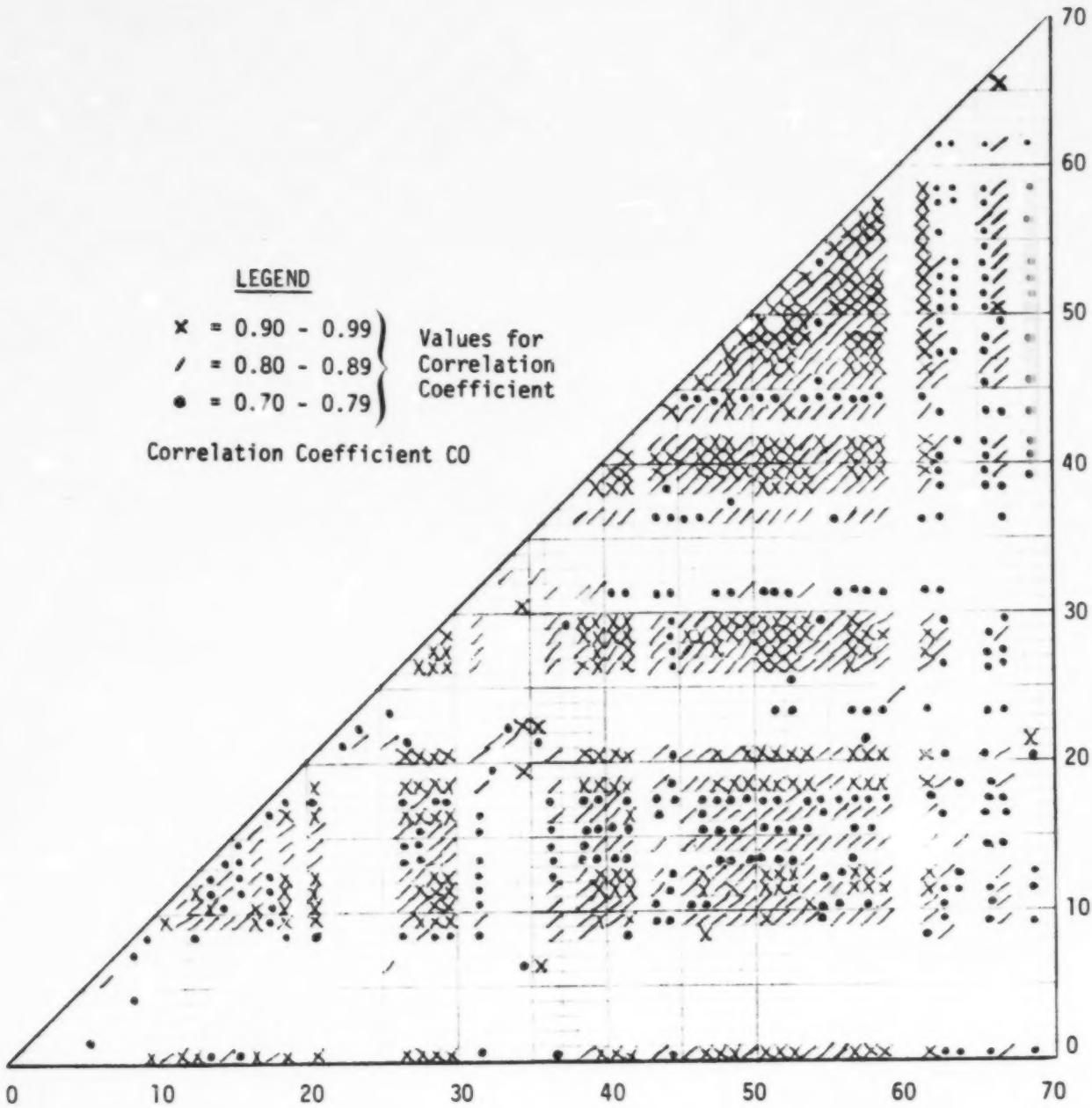

Figure 22. Pairwise Correlation Matrix - Scott Data

TABLE 9

CODED COMPOUNDS - SCOTT DATA

1. Carbon Monoxide
2. Oxidants
3. Blank
4. Total Hydrocarbons
5. Wind Speed
6. Temperature
7. Relative humidity
8. Wind direction
9. UV flux
10. Methane
11. Ethane
12. Ethylene
13. Acetylene
14. Propane
15. Propylene
16. Isobutane
17. Butane
18. Butanes
19. Isopentane
20. 1-Pentene + 2-Methyl-1-Butene
21. n-Pentane
22. trans-2-Pentene
23. cis-2-Pentene
24. 2-Methyl-2-butene
25. 2,2-Dimethylbutane
26. Cyclopentene
27. Cyclopentane
28. 2,3-Dimethylbutane
29. 2-Methylpentane
30. 3-Methylpentane
31. 1-Hexene
32. n-Hexane
33. trans-3-Hexene
34. trans-2-Hexene
35. cis-3-Hexene
36. cis-2-Hexene
37. Methylcyclopentane
38. 2,4-Dimethylpentane
39. Benzene + Cyclohexane
40. 2-Methylhexane + 2,3-Dimethylpentane
41. 3-Methylhexane
42. 2,2,4-Trimethylpentane
43. 1-Heptene + ?
44. n-Heptane
45. Methylcyclohexane
46. 2,4-Dimethylhexane
47. 2,5-Dimethylhexane
48. 2,3,4-Trimethylpentane
49. Toluene
50. n-Octane
51. Ethylbenzene
52. m + p-Xylene
53. o-Xylene
54. n-Nonane
55. Isopropylbenzene
56. n-Propylbenzene
57. 4-Ethyltoluene
58. 3-Ethyltoluene
59. 1,3,5-Trimethylbenzene
60. 2-Ethyltoluene
61. tert-Butylbenzene
62. 1,2,4-Trimethylbenzene
63. n-Decane
64. sec-Butylbenzene
65. Isobutylbenzene
66. n-Butylbenzene
67. n-Undecane
68. Nitrogen Dioxide
69. Nitric Oxide

Walden

The apparent lack of correlation between a number of hydrocarbon species (Codes Nos. 19, 22-26, 33-36, 60-61) can be partly attributed to a low number of samples for these components.

SECTION VIII

CITED REFERENCES

1. Wayne, L., Danchick, R., Weisburd, M., Kokin, A., and Stein, A., "Modeling Photochemical Smog on a Computer for Decision Making", Presented at Annual Meeting, APCA, St. Louis, June 14-19 (1970).

2. Lamb, R.G., An Air Pollution Model of Los Angeles, M.S. Thesis, UCLA (1968).

3. Eschenroeder, A., and Martinez, J., A Modeling Study to Characterize Photochemical Atmospheric Reactions to the Los Angeles Basin Area, General Research Corporation CR-1-152 (November 1969).

4. Scott Research Laboratories, Final Report on Phase I, Atmospheric Reaction Studies in the Los Angeles Basin, Vol. I and II (1969).

5. Lemke, E.E., Thomas, G., and Zwiacher, W.E. (eds.), "Profile of Air Pollution Control in Los Angeles County", County of Los Angeles Air Pollution Control District (1969).

6. Neligan, R.E., Mader, P.P., and Chambers, L.A., "Exhaust Composition in Relation to Fuel Chemistry", J. APCA, 11, 178 (1961).

7. Stephens, E.R., and Burleson, F.R., "Analysis of the Atmosphere for Light Hydrocarbons", J. APCA, 17, 147 (1967).

8. Gordon, R., Mayrsohn, H., and Ingels, R., "$C_2 - C_5$ Hydrocarbons in the Los Angeles Atmosphere", Envir. Sci. Tech., 2, 1117 (1968).

9. Lonneman, W.A., Bellar, T.A., and Altshuller, A., "Aromatic Hydrocarbons in the Atmosphere of the Los Angeles Basin", Envir. Sci. Tech., 2, 1017 (1968).

10. Koehl, W.J., Jr., "Mathematical Models for Prediction of Fuel Tank and Carbureator Evaporative Losses", SAE Paper 690506 (May 1969).

11. Scott Research Laboratories, "Investigation of Passenger Car Refueling Losses" (March 1970).

12. Eschenroeder, A., and Martinez, J., Analysis of Los Angeles Atmospheric Reaction Data from 1968 and 1969, Draft Report (July 1970).

13. Friedlander, S.K., and Seinfeld, J.H., "A Dynamic Model of Photochemical Smog", Envir. Sci. Tech., 3, 1175 (1969).

14. Altshuller, A.P., "An Evaluation of Techniques for the Determination of the Photochemical Reactivity of Organic Emissions", J. APCA, 16, No. 5, 257 (1966).

15. Altshuller, A.P., and Bufalini, J.J., "Photochemical Aspects of Air Pollution: A Review", Envir. Sci. Tech., 5, 29 (1971).

16. Whittaker, E., and Robinson, G., The Calculus of Observations, 4th Edition, Dover Publications, New York (1967).

17. Altshuller, A.P., Kopczynski, S.L., Wilson, D., Lonneman, W., and Sutterfield, F.D., "Photochemical Reactivities of N-Butane and other Paraffinic Hydrocarbons", J. APCA, 19, 787 (1969).

18. Kopczynski, S.L., Lonneman, W.A., Sutterfield, E.D., and Darley, P.E., "Photochemical Reactivity of the Los Angeles Atmosphere", Presented at 62nd Annual Meeting, APCA, New York, June 22-26, 1969.

19. Schuck, E.A., Altshuller, A.P., Barth, D.S., and Morgan, G.B., "Relationship of Hydrocarbons to Oxidants in Ambient Atmospheres", J. APCA, 20, 297 (1970).

20. Mayrsohn, H., et al., "Second Street Tunnel Study", California Air Resources Board (January 1971).

21. Maynard, J., and Sanders, W., "Determination of the Detailed Hydrocarbon Composition and Potential Atmospheric Reactivity of Full-Range Motor Casones", J. APCA, 19, 505 (1969).

22. Nelson, E.E., "Hydrocarbon Control for Los Angeles by Reeucing Gasoline Volatility", SAE Paper 690087 (January 1969).

23. Danielson, J.A., Edit., Air Pollution Engineering Manual, EPA, May 1973.

24. Papa, L.J., "Gas Chromatography — Measuring Exhaust Hydrocarbons Down to Parts per Billion", SAE Paper 670494 (May 1967).

25. Bonamassa, F., and Wong-Woo, H., "Composition and Reactivity of Exhaust Hydrocarbons from 1966 California Cars" (September 1966).

26. Eccleston, B.H., Noble, B.F., and Hurn, R.W., "Influence of Volatile Fuel Components on Vehicle Emissions, U.S. Bureau of Mines, R.I.7291 (1970).

27. Dickinson, G.W., et.al., "Tune-Up Inspection - A Continuing Emission Control", SAE Paper 690141 (January 1969).

28. Roberts, P.J.W., Roth, P.M., and Nelson, C.M., Report 71 SAI-6, Systems Applications, Inc., for the Air Pollution Control Office, Environmental Protection Administration, under Contract CPA 70-148 (1971).

29. Colucci, J.M., and Begeman, C.R., APCA Paper No. 67-182, presented at annual meeting, Air Pollution Control Asscciation, Cleveland, Ohio (June 1967).